ERRATA

Due to an oversight in the second printing, three lines have been omitted from the bottom of page 92. These should read:

priority is discussed in a thorough manner in Dr. Jörgensen's book, "*Die Entdeckung des Sauerstoffes*," which was translated from Danish into German by Ortwed and Speter.

Frontispiece to the German Translation of
P.-J. Macquer's "Dictionnaire de Chymie," 1788

DISCOVERY OF THE ELEMENTS

by

MARY ELVIRA WEEKS

Research Associate in Scientific Literature at the Kresge-Hooker Scientific Library, Wayne University. With illustrations collected by F. B. Daines, Professor of Chemistry at the University of Kansas

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FOREWORD

The material blessings that man enjoys today have resulted largely from his ever-increasing knowledge of about ninety simple substances, the chemical elements, most of which were entirely unknown to ancient civilizations. In the luxurious thermæ of the Roman patrician, with all their lavish display of alabaster floors, porphyry walls, marble stairs, and mosaic ceilings, no nickel-plated or chromium fixtures were to be seen; among his artistic golden bowls and goblets no platinum or tantalum objects were ever to be found; with all his spoils of war he could not buy the smallest aluminum trinket.

Even the haughtiest Roman conqueror was earthbound, for he knew no light metal like aluminum or magnesium and no light gas like hydrogen or helium to make lofty flight possible. Without a lantern in his hand, he could not walk along the splendid lava pavements of the city streets at night, for the white glow of the tungsten filament and the crimson glow of the neon tube were lacking. The water that came to him from mountain springs, lakes, and rivers through miles of magnificent aqueducts was a menace to health, for there was no chlorine with which to kill the bacteria. When accident befell him, there was no iodine for the healing of the wound; when he lay gasping for breath, no cylinder of oxygen to save him.

The story of the disclosure, one by one, of the chemical elements has never been told as a connected narrative. The reports of these discoveries and the life stories of the discoverers are recorded for the most part in old chemical journals, biographical dictionaries, old letters, and obsolete textbooks that are seldom read by the busy modern chemist. It is hoped, therefore, that these chapters may not only render tribute to the honored men and women who helped to reveal the hidden chemical elements, but that they may also serve to acquaint chemists and others with these great achievements.

The task of selecting and eliminating material has been pleasant but difficult. It has frequently happened that two or more men have discovered the same element independently. In other instances various observers have recognized the existence of a new element long before it was actually isolated. In such cases an attempt has been made to relate all important steps in the discovery as fairly and completely as possible without ascribing the honor of discovery to any one person.

. . . . . .

It is a pleasure to acknowledge the kind assistance given by the late Dr. E. H. S. Bailey and Dr. Selma Gottlieb Kallis, who read portions of the manuscript, by Dr. F. B. Dains, who made many helpful suggestions as to sources of material and furnished most of the illustrations, and by the late Dr. Max Speter, who read the proof for the fourth edition.

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THE DISCOVERY OF THE ELEMENTS

I. ELEMENTS KNOWN TO THE ANCIENT WORLD

Although the ancient conception of an element was quite different from the modern one, a few of the substances now recognized as chemical elements have been known and used since the dawn of history. Although no one knows who discovered these ancient "building-stones of the universe," the writings of Pliny the Elder and Dioscorides and the Hebrew and Hindu Scriptures abound in interesting allusions to the metals, gold, silver, copper, iron, lead, tin, and mercury, and the non-metals, sulfur and carbon.

> "*The world of chemical reactions is like a stage, on which scene after scene is ceaselessly played. The actors on it are the elements*" (*1*).

rom Delbrueck's "Antike Porträts"

HERACLITUS, 540–475 B.C.

Ascetic Greek philosopher and founder of metaphysics. He believed that fire is the primary substance, and that change is the only actuality in Nature.

The chemical elements, those primeval building materials from which Nature has constructed all her varied forms, have been discovered, one by one, through the ages, by patient searchers in many lands. The ancient

Seventeenth-Century Symbol for Iron

(*From Peters' "Aus pharmazeutischer Vorzeit in Bild und Wort"*)

Seventeenth-Century Symbol for Silver

(*From Peters' "Aus pharmazeutischer Vorzeit in Bild und Wort"*)

Greek philosophers, Thales, Xenophanes, and Heraclitus, believed that all substances were composed of a single element, but they did not agree as to its nature. Thales thought that water was the element which, upon evaporating and condensing, produced all substances. Heraclitus, however, believed that fire was the one fundamental building material.

The conception of four simple substances (earth, air, water, and fire) had its origin in the mind of Empedocles about four hundred and forty years before the birth of Christ, and held sway for many centuries. Every one knows today that neither earth nor air, water nor fire is an element. Earth is the most complex of all, for it can be separated into many chemical compounds, whose natures vary according to the locality from which the soil has been taken. From air can be obtained a number of simple gases, among them nitrogen, oxygen, and argon. Water, also, can be easily decomposed into the two gaseous elements, oxygen and hydrogen; and fire, far from being an element, consists of the incandescent gases or glowing embers of the fuel which is being burned. Simple as these facts may seem to the modern mind, the world's best intellects once debated them and established them. During the centuries, man's conception of what constitutes a chemical element has undergone many other changes, which were ably discussed by the late B. N. Menschutkin in the *Journal of Chemical Education* for February, 1937 (*82*).

PLINY THE ELDER, 23–79 A.D.
Roman philosopher. Author of a "Natural History" in 37 books, in which he discussed the astronomy, geology, zoölogy, botany, agriculture, mineralogy, and medicine of his time.

The story of the "defunct elements," those short-lived "elements" which were later found to be complex, is most interesting, but the present narrative will be confined to the simple substances now recognized by chemists. The curious false elements, considerably more than a hundred in number, have been described in a fascinating article by the late Charles Baskerville (*2*).

The chemical elements which were undoubtedly known to the ancient world are the metals: gold, silver, copper, iron, lead, tin, and mercury, and the non-metals: sulfur and carbon. The ancient Jews, as one learns from the Old Testament, were certainly acquainted with the first four of these metals, and probably with the first six. The ancient Hindus used them also, for Sir Praphulla Chandra Rây quotes from the Charaka: "Gold and the five metals . . . silver, copper, lead, tin, and iron" (*3*).

Ancient Metals

Gold ornaments have been found in Egyptian tombs of the prehistoric stone age, and the Egyptian goldsmiths of the earliest dynasties were skilful artisans. The metal was used as a medium of exchange in the days of Abraham, and is mentioned in Exodus, Deuteronomy, the First Book of Kings, Job, the Psalms, the Proverbs, Isaiah, Lamentations, Haggai, and Zechariah (*4*). Pliny the Elder (A.D. 23–79) said that grains of gold were found in the stream-beds of the Tagus in Spain, the Po in Italy, the Hebrus in Thracia, the Pactolus in Asia Minor, and the Ganges in India (*5*). In the second century before Christ, a cupellation process was used for refining the metal, and in Pliny's time the mercury process was well known (*6*).

From Biringuccio's "Pirotechnia"

AN ASSAY FURNACE, 1540

Vitruvius, who lived in the reign of Augustus, mentioned the use of mercury to recover finely divided gold. "When gold has been woven into a garment," said he, "and the garment becomes worn out with age so that it is no longer respectable to use, the pieces of cloth are put into earthern pots, and burned up over a fire. The ashes are then thrown into water and quicksilver added thereto. This attracts all the bits of gold, and makes them combine with itself. The water is then poured off, and emptied into a cloth and squeezed in the hands, whereupon the quicksilver, being a liquid, escapes through the loose texture of the cloth, but the gold, which has been brought together by the squeezing, is found inside in a pure state" (*47*).

Silver, since it rarely occurs uncombined, did not come into use as early as did gold (*29*). In Egypt between the thirtieth and fifteenth centuries before Christ, it was rarer and more costly than gold. It must have been used as a medium of exchange long before it was coined, for it is related in Genesis that when Abraham purchased a burial place for Sarah he weighed out the silver in the presence of witnesses (*7*). Jagnaux states that when the Phœnicians made their first voyage to Spain they found more silver than their ships could carry, and that, for this reason, they weighted their wooden anchors with silver instead of lead (*8*). When the Spaniards conquered Peru they found many silver utensils that had been made by the ancient inhabitants (*9*), (*28*).

In his "Natural and Moral History of the Indies," Father José de Acosta wrote in 1590: "The Creator hath furnished the West Indies with so great a treasure of silver, as all that which we reade of in antient Histories and that which is spoken of the mines of Spaine, and other provinces, is not comparable to that we see in those partes.... The maner to purge and refine siluer (sic) which the Indians have vsed was by melting, in dissolving this masse of mettall by fire, which casts the earthly drosse aparte, and by his force separates silver from lead, tinne from copper, and other mettalls mixt.

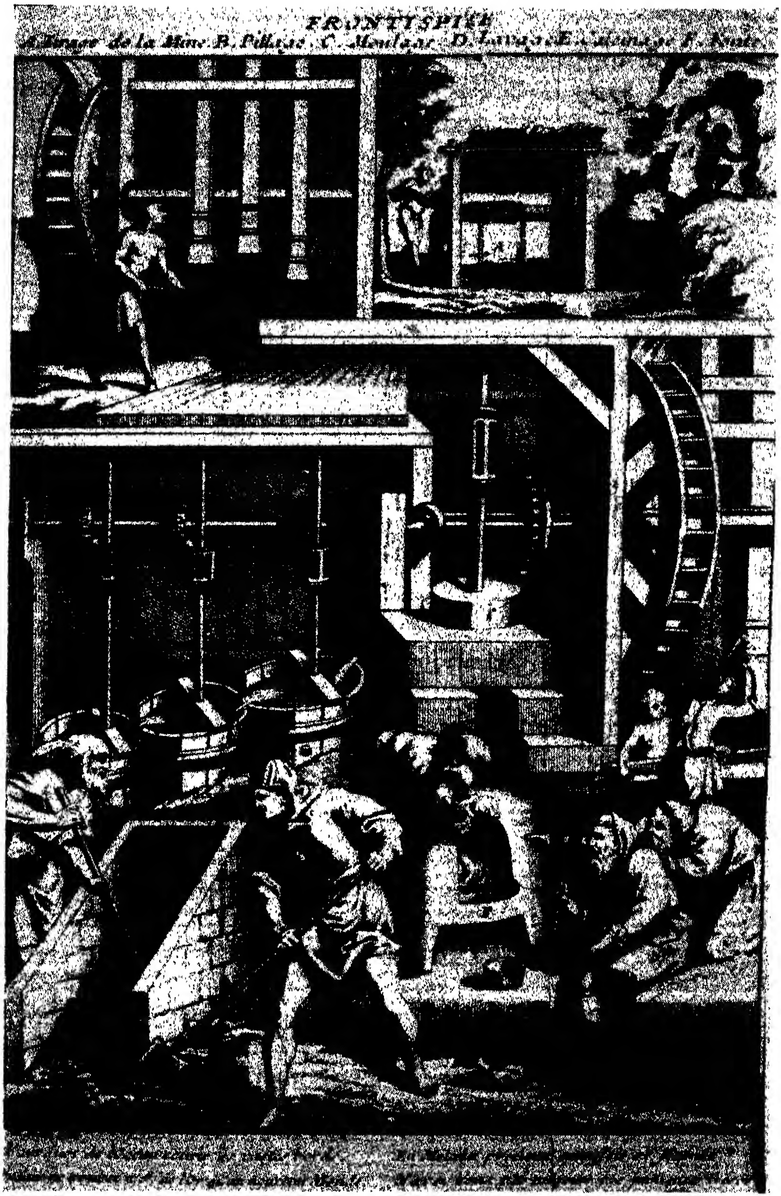
"To this end," continued Father de Acosta, "they did build small furnaces in places whereas the wind did commonly blow, and with wood and cole made their refining, the which furnaces in Peru they call *huayras*. Since the Spaniards entred, besides this manner of refining which they vse to this day, they likewise refine silver with qvick-silver, and draw more by this means then (sic) in refining it by fire. For there is some kind of silver mettal found which can by no means be purged and refined by fire, but onely with quicksilver..." (*45*).

According to Father de Acosta, "the chief places of the Indies from which they draw silver are New Spaine [Mexico] and Peru; but the mines of Peru farre surpasse the rest; and amongst all others of the worlde, those of Potosí [now in Bolivia]" (*45*). "At this day," he said, "the most vsuall maner of refining in Potosí is by quickesilver, as also in the mines of Zacatecas, and others of New Spaine. There were in old time, vpon the sides and toppes of Potosí, above six thousand *Huayras*, which are small furnaces where they melt their mettall, the which were placed like lightes (a pleasant sight to behold by night) casting a light a farre off like a flame of fire.... But at this day there are not above two thousand.. " (*45*).

Of the assay-masters, Father de Acosta said, "Their ballaunce and weights are so delicate, and their graines so small, as they cannot take them vppe with the hand, but with a small paire of pincers: and this triall they make by candle light, that no ayre might moove the ballance. For of this little the price of the whole barre dependeth" (*45*).

In the seventeenth century, Father Alvaro Alonso Barba of Potosí said that some of the mines there had been worked by the Incas and that, since the coming of the Spaniards, the wealth of this hill had been distributed to all parts of the world (*46*).

Copper, in the opinion of Berthelot, has been mined for at least five



J. B. Scolin, sculp.

FRONTISPIECE TO 1733 FRENCH EDITION OF BARBA'S "ART OF THE METALS"

The poem mentions that France used to be rich in precious metals, and questions the necessity of searching for them in the New World.

> Pourquoi de l'Océan courir les vastes bords.
> France, ne trouvez vo? de l'Or qu'au nouveau Monde.
> En Métaux précieux autrefois si féconde,
> N'avez vous pas toujours vos immenses Trésors.

thousand years. He found by analysis that the most ancient Egyptian articles were made of pure copper rather than of its alloys (*10*), (*27*). "Two vessels of fine copper, precious as gold" were mentioned by the prophet Ezra (*11*). This metal is found in the free state in Egypt, the Lake Superior region of North America, and in many other parts of the world, and can be obtained from malachite ore by a simple process.

Knives, axes, spear heads, chisels, and bracelets of this metal have been found in Indian mounds in Wisconsin, Illinois, and neighboring states. Indian tools and excavations for working the copper veins have been discovered in the Ontonagon region of northern Michigan (*39*). Much of the copper worked by the aborigines came from Isle Royale in Lake Superior (*40*).

The pre-Columbian Indians of La Tolita on the Esmeraldas coast of Ecuador made small axes, bells, sewing needles, and filigree work by hot-hammering native copper. Paul Bergsøe of Copenhagen has made a thorough study of the gold, platinum, and copper artifacts of this region (*41*).

Arriving at last in the fabled Quivira (now part of Kansas) after his remarkable journey from Compostela, Mexico, in search of the gold and silver treasures described by his false guide "the Turk," Don Francisco Vázquez de Coronado wrote King Charles V on October 20, 1541, that "the natives there gave me a piece of copper that an Indian chief wore suspended from his neck. I am sending it to the viceroy of New Spain, for I have not seen any other metal in this region except this and some copper jingle bells which I am forwarding to him" (*42*). In his treatise on the Coronado expedition, George Parker Winship stated that Indian traders used to carry pieces of copper from the mines on the shores of Lake Superior, from tribe to tribe, as far east as the Atlantic Ocean and as far west as the Rocky Mountains (*43*).

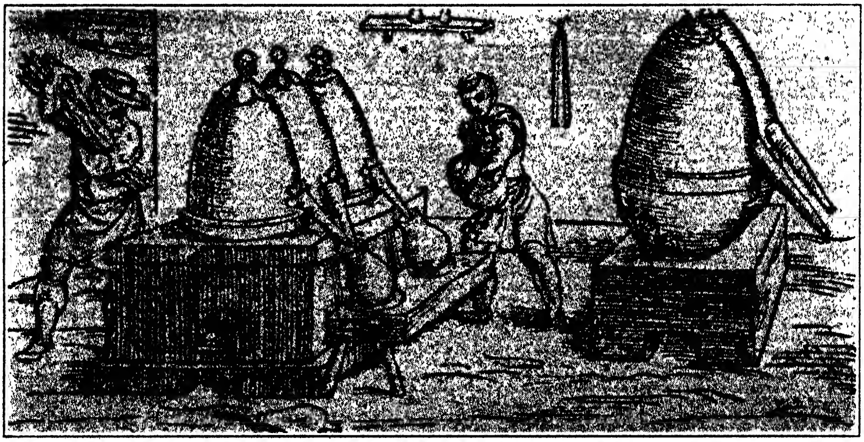
In describing his voyage to northern Virginia with Sir Walter Raleigh, John Brereton wrote in 1602 that he had seen Indians wearing elaborate chains, earrings, and collars of copper, and that some of their arrow heads and skull-shaped drinking cups were made of it (*44*).

Iron articles were probably made by the Egyptians twenty-five or thirty centuries before Christ, but because the metal is so readily corroded, iron objects of great antiquity are much rarer than similar ones made of gold, silver, or copper (*25*). Smelting furnaces for iron were used in ancient times, but the exact nature of the process is not known. The metal must have been in common use in Pliny's day, for he wrote (*12*):

> It is by the aid of iron that we construct houses, cleave rocks, and perform so many other useful offices of life. But it is with iron also that wars, murders, and robberies are effected, and this, not only hand to hand, but from a distance even, by the aid of weapons and winged

> weapons, now launched from engines, now hurled by the human arm, and now furnished with feathery wings. This last I regard as the most criminal artifice that has been devised by the human mind; for, as if to bring death upon man with still greater rapidity, we have given wings to iron and taught it to fly. Let us, therefore, acquit Nature of a charge that belongs to man himself. . . . . Nature, in conformity with her usual benevolence, has limited the power of iron by inflicting upon it the punishment of rust; and has thus displayed her usual foresight in rendering nothing in existence more perishable than the substance which brings the greatest dangers upon perishable mortality.

Of all the ancient allusions to this metal, the Biblical ones are the most interesting. Who can forget Job's eloquent words: "Oh, that my words were now written! Oh, that they were printed in a book! That they were graven with an iron pen . . . . ." (*13*). In Deuteronomy one may read with surprise of Og, that giant king of Bashan who slept in an iron bed six feet wide and thirteen and one-half feet long (4 × 9 cubits)! (*14*). This "bed" was probably a sarcophagus (*37*), (*38*), or possibly a natural rock formation of black basalt (*48*).



From Biringuccio's "Pirotechnia"

MERCURY STILLS, 1540

G. W. Wainwright regards some iron beads which he found at Gerzah, Egypt, about fifty miles south of Cairo, as the most ancient pieces of iron known. They date back to 3500 B.C. or earlier. Since they contain 7.5 per cent of nickel, they must have been made from meteoric material (*77*). Primitive tribes often used meteoric iron for weapons and tools, and, because of its celestial origin, regarded it with great reverence. Under the title "Our Stone-pelted Planet," H. H. Nininger has published a scholarly and entertaining history of the most famous meteorites (*78*).

The earliest known finds of smelted iron are from Tell Asmai, Mesopotamia, and Tall Chagar Bazaar in North Syria. One such specimen cannot have been made later than 2700 B.C. and may have been produced as early as 3000 B.C. Since it contains no nickel, it cannot be of meteoric origin (*79*). Although the Hittites developed skill in smelting iron, they kept the process secret. After the fall of their Empire shortly before 1200 B.C., the iron workers were dispersed and the true Iron Age dawned in the Near East. About two centuries later, according to H. H. Coghlan, this craft reached Europe (*79*).

Many Negro tribes of Africa have worked iron for centuries. In his "Mining and Metallurgy in Negro Africa," Walter Cline states that the iron and slag found in the earliest deposits at Zimbabwe give evidence that iron must have been smelted in southeast Africa at least as early as the eighth century A.D. and that by that time the "iron age" in this locality was well advanced (*80*). According to A. F. Cronstedt, the process of making osmund iron was known to the Eskimos, Yakuts, and Ostiaks of Siberia (*81*).

Lead ores are widely distributed in Nature, and are easily smelted. The Babylonians engraved inscriptions on thin plates of metallic lead (*10*), and references to this metal are also found in Exodus, Numbers, and Jeremiah. The Romans used it extensively for water-pipes, writing-tablets, and coins. Unfortunately, they also used it for cooking utensils, and lead poisoning was an all-too-frequent result. A few very small lead nuggets, some of which are believed to be of pre-Columbian origin, have been found in Peru, Yucatan, and Guatemala (*41*).

Although tin bronzes were made thirty centuries before Christ, it is not certain that metallic tin was known to the ancients. The prophet Ezekiel mentioned it in the following passage: "Tarshish was thy merchant by reason of the multitude of all kind of riches; with silver, iron, tin and lead, they traded in thy fairs" (*15*).

Since cassiterite is the only important ore of tin, it must have been the earliest source of the metal. Although the Cassiterides, or tin islands, mentioned by classical writers were usually supposed to have been named for the ore, cassiterite may possibly have been named for the islands, just as copper was named for Cyprus and bronze for Brundisium (Brindisi, Italy) (*62*). In speaking of mirrors, Pliny the Elder stated that "the best known to our forefathers were made at Brundisium from a mixture of copper and *stagnum*" (*63*).

The composition of Peruvian bronze, according to Hiram Bingham, was not accidental. Pure tin which had evidently been prepared for use in casting was found at Machu Picchu, the mountain citadel of the Incas. The ancient inhabitants of this fortress were highly skilled metallurgists who made bronze implements of varying composition according to the purposes for which they were to be used. No artifacts of pure tin were found there (*64*).

In his "Ancient Egyptian Materials and Industries," A. Lucas states that, although tin ore has not been found in Egypt, the earliest known artifacts of this metal, apart from bronze, are a ring and a pilgrim bottle from Egyptian tombs of the eighteenth dynasty (1580 B.C. to 1350 B.C.) (*65*).

Homer's "Iliad" relates how Hephaistos, the lame god of fire, made a shield for Achilles: "And he threw bronze that weareth not into the fire, and tin and precious gold and silver...." Among the many decorations on the shield was a vineyard scene in gold and silver with a fence of tin and a herd of cattle, "and the kine were fashioned of gold and tin...." The greaves were of "pliant tin" (*66*). This may have been a tin alloy, however, rather than the pure metal (*62*).

Herodotus (484–425 B.C.) said in his "History" that he did not know of any "islands called the Cassiterides whence the tin comes which we use....Though I have taken great pains, I have never been able to get an assurance from an eye-witness that there is any sea on the further side of Europe. Nevertheless, tin and amber do certainly come to us from the ends of the earth" (*67*).

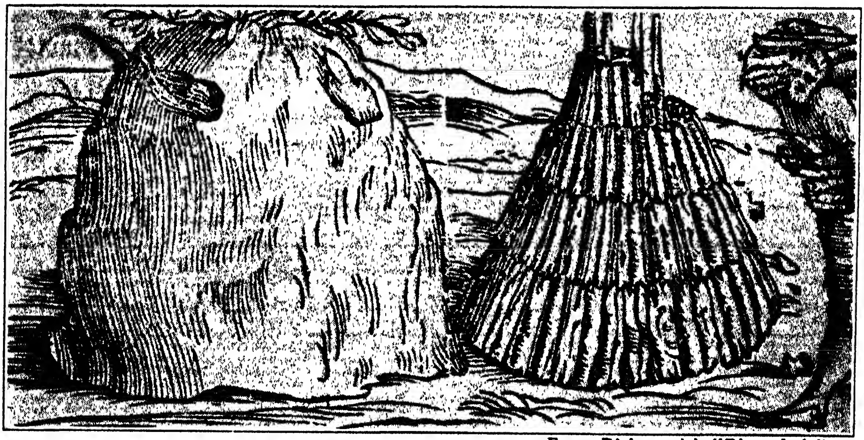
WOODCUT SHOWING DISTILLATION OF SULFUR IN 1557

In his valuable book entitled "The Cornish Miner," A. K. H. Jenkin mentions some excavations made in 1925 at the famous castle of Chun, near St. Just, which dates back to 300 to 200 B.C. The slag found in the small smelting-pits there contained tin. Thus the Cornish tin industry must be more than two thousand years old. The earliest known charter of the Cornish stannaries is dated 1201 (*68*). In Book V of his "Commentaries on the Gallic War," Julius Caesar mentioned the production of tin in the midland regions of Britain (*69*).

In the first century of the present era, the Latins referred to tin as "plumbum album" to distinguish it from lead, which they called "plumbum nigrum" (*16*). Pliny and Dioscorides mentioned the use of tin coatings to prevent corrosion of copper vessels (*17*).

When Hernando Cortes arrived in Mexico, tin from a mine in Taxco was already in circulation as money (*40*), (*70*). "Some small pieces of it," said Cortes, "were found among the natives of a province called Tachco [Tasco, or Taxco], in the form of very thin coins; and continuing my search I discovered that in that province and many others this was used as money; I further learned that it was mined in the province of Tachco, twenty-six leagues from this city [Temixtitan]" (*71*).

Mercury was known to the ancient Chinese and Hindus, and has been found in Egyptian tombs dating back to 1500 or 1600 B.C. (*10*). Dioscorides mentioned its preparation from cinnabar (*18*), while Pliny gave a method of purifying it by squeezing it through leather, and stated that it is poisonous (*6*). Earle R. Caley has shown by quotations from Aristotle, Theophrastus, Dioscorides, Pliny the Elder, Vitruvius, and the Leyden Papyrus of the third century A.D. that mercury has been known much longer than most persons realize. He states that cinnabar was probably the only mercury compound known to the ancients and that they used it both as a pigment and as a source of the metal (*49*). In his "Metallurgic Chemistry," C. E. Gellert (1713–1795) stated that "The only ore of mercury hitherto known is native cinnabar" (*50*). The most ancient specimen of quicksilver known is probably that which H. Schliemann found in a little cocoanut-shaped amulet in an Egyptian tomb at Kurna dating from the fifteenth or sixteenth century B.C. (*51*), (*52*).



From Biringuccio's "Pirotechnia"

MANUFACTURE OF WOOD CHARCOAL

Theophrastus, a disciple of Plato and successor to Aristotle, described quicksilver as a useful substance "obtained from native Cinnabar, rubbed with Vinegar in a brass Mortar with a brass Pestle" (*53*), (*54*), (*55*).

In the first century A.D., Dioscorides Pedanius of Anazarbus, Cilicia, gave the following process for preparing metallic mercury: "Putting an iron spoon having Cinnabaris in an earthen pot, they cover the Cup, dawbing it about with clay, then they make a fire under with coals; and ye soot that sticks to ye pot, being scraped off & cooled, becomes Hydrargyrum [mercury]. It is found also in ye place where Silver is melted, standing together by drops on ye roofs. And some say that Hydrargyrum is found by itself in ye mines. But it is kept in glassen, or leaden, or tinnen, or silver vessels, for it eats through all other matter, and makes it run out" (*18*), (*56*).

The Chinese alchemist Ko Hung (281–361 A.D.) wrote in the Pao Pu Tzu, "Many do not even know that mercury comes out of cinnabar (*tan sha*). When told, they still refuse to believe it, saying that cinnabar is red, and how can it produce a white substance? They also say that cinnabar is a stone—that stones when heated turn to ashes: and how then can anything else be expected of *tan sha?*" (*57*).

J. M. Hoppensack stated in 1795 that the mercury mines of Almadén had been worked for at least 2287 years and that cinnabar from them was sent to ancient Rome in the form of powder or sand (*58*). A. de Gálvez-Cañero believes that the Spanish mercury mines have been worked since the third or fourth century B.C. (*28*).

In his "Natural and Moral History of the Indies," Father José de Acosta said that the Incas labored long in the Peruvian mercury mines without knowing what quicksilver was, seeking only cinnabar, or vermilion, to use as war paint (*59*). The Spaniards discovered the mercury mines of Huancavelica in 1566–67. When Pedro Fernándes de Velasco demonstrated his cold amalgamation process in 1570 to the Viceroy, the latter offered him suitable reward, ordered him to make the secret known at Potosí (Bolivia), and added that the most important wedding in the world was about to take place: the marriage of Mount Potosí (silver) to Mount Huancavelica (mercury) (*60*). A description of the Spanish and the Peruvian quicksilver mines was published in the *American Journal of Science* for 1868 (*61*).

Ancient Non-Metals

Since sulfur and carbon both occur uncombined in many parts of the world they must certainly have been known to all the ancient peoples. After the killing of the wooers in Book XXII of Homer's "Odyssey," Odysseus called to Eurycleia, "Bring sulphur, old nurse, that cleanses all pollution and bring me fire, that I may purify the house with sulphur" (*72*). Pliny described the Italian and Sicilian deposits in great detail, mentioning the use of block sulfur for medicinal purposes, the bleaching of cloth with sulfur vapor, and the manufacture of sulfur matches and lamp-wicks (*19*), (*73*). Georgius Agricola (*26*) stated that these matches could be ignited by friction on stone and used for lighting candles and dry wood. He also left no doubt as to his opinion of gunpowder when he said: "Sulfur is also made to enter into that powder—execrable invention—which hurls iron, brass, or stone instruments of war of a new kind" (*20*).

It is difficult for the modern chemist to understand the early literature of sulfur, for the name was incorrectly used to designate all combustible substances. In the eighth century, Geber believed that the metals were compounds of sulfur and mercury; and hence these two elements came to have great significance for the alchemists. Abu Mansur mentioned the use of the former as an antidote for various kinds of metallic poisoning, and Pseudo-Geber told how to prepare milk of sulfur by adding vinegar to alkaline sulfur solutions (*34*). Some scholars regard the Latin work "Invention of Verity, or Perfection," as a translation of an unknown Arabic treatise by Geber (Abu Musa Jabir ibn Hayyan), who lived in the eighth century A.D. Professor Julius Ruska believes, however, that Geber (Jabir) and Pseudo-Geber (the author of the "Invention of Verity") must have been separated by five centuries of time (*35*).

From Bugge's "Das Buch der grossen Chemiker"

GEORGIUS AGRICOLA, 1494–1555

German metallurgist. Author of "*De Re Metallica*," a famous Latin treatise on mining and metallurgy, which has been translated into English by Ex-president and the late Mrs. Herbert Hoover.

The sulfur from which Cortes and his daring conquistadores made their first gunpowder was obtained, so he said, from the rumbling, smoking crater of Mount Popocatepetl (*70*). In a letter to Charles V, written from Temixtitan on October 15, 1524, he said, "As for sulphur, I have spoken to Your Majesty of that mountain in the province of Mexico which smokes. A Spaniard [Francisco Montaño] descended by means of a rope, seventy or eighty fathoms, and obtained a sufficient quantity to last us in our need; but henceforward there will be no necessity of going to this trouble because it is dangerous and I shall always write to obtain these things from Spain" (*76*).

In 1759 Count Vincenzo Masini (1689–1762) of Cesena, Italy, published a patriotic poem on sulfur, in which he described its extraction, purification, and uses. Signor Gino Testi has published extracts from this poem, with explanatory notes (*74*). In eloquent Italian verses Count Masini gave poetic expression to Giorgio Baglivi's belief that vegetables and animals exert an influence over the formation of the metals and the so-called semimetals

"...*Within the rocks, among the thorns,*
Between the cliffs, sulfur takes root;
For gold, silver, copper, iron, and sulfur
Likewise are plants" (*74*)*

Count Masini also dramatically expressed the relation between sulfur and volcanic action.

The Abbé Lazaro Spallanzani (1729–1799) described the sulfurous fumes of Vulcano, and added that "Above these fumes there is a plain, of no great extent, which one is at first afraid to venture on, from the subterranean noise heard there, and from the shaking of the ground when struck with the foot.... On this plain it was that formerly stood the furnaces in which the sulphur of Vulcano was purified. But this useful labour has long since been abandoned...nor was it abandoned because the quantity of sulphur obtained was too little..., as the vein is very rich and even inexhaustible. The real cause why the inhabitants of Lipari no longer continued this work was that the ground...grows hotter the deeper it is dug into..., to which is to be added the offensive stench of the sulphureous fumes... " (*75*).

In the latter part of the eighteenth century, A. L. Lavoisier and his adherents regarded sulfur as an element. As late as 1809, however, Sir Humphry Davy believed that it contained oxygen and hydrogen as essential constituents and that it was similar in composition to the resins (*30*), (*33*). Experiments by A. Berthollet, son of C. L. Berthollet, had indicated that sulfur contains hydrogen. From his own experiments with Sicilian sulfur in 1808, Sir Humphry concluded that "the existence of hydrogen in sulphur is fully proved" and that "sulphur, in its common state, is a compound of small quantities of oxygen and hydrogen with a large quantity of a basis that produces the acids of sulphur in combustion..." (*30*). In 1809 Gay-Lussac and Thenard thoroughly established the elementary nature of sulfur (*31*), (*32*).

By 1810 Davy had changed his views and suspected "a notable proportion of oxygen in Sicilian sulphur, which is probably owing to the presence of oxide of sulphur.... Considering the manner in which sulphur is procured in Sicily, it might be expected to contain oxygen; when taken from the mine, the limestone rock containing it, broken into small fragments, is subjected to heat in a kind of kiln; whilst a small portion of the sulphur is

---

* "...*Entro le balze*
Fra dumi, e fra dirupi il zolfo aligna;
Che piante e vegetabili pur sono
L'oro, l'argento, il rame, il ferro, il zolfo..." (*74*)

burnt, and ascends into the atmosphere in the form of sulphurous acid gas, the greater part of it melts, sinks, and flows out through an opening designed to give issue. This process I witnessed at the extensive sulphur mines in the neighbourhood of Gujenti [Girgenti, or Agrigentum]; and I believe it is generally in use throughout the sulphur districts" (*30*).

When Davy allowed "oxymuriatic acid gas" (chlorine) to react with moist sulfur, he obtained hydrogen chloride and oxygen. When he repeated the experiment, using Sicilian sulfur dried over calcium chloride, "no oxygen gas was evolved and not a cubical inch of muriatic [hydrochloric] acid...and it was found that between 16 and 17 cubical inches of oxymuriatic acid gas [chlorine] had disappeared; the whole of the sulfur was sublimed in the gas, and the liquor formed was of a tawny-orange colour" [probably sulfur monochloride] (*30*).

Carbon in the forms of charcoal and soot must certainly have been known even to prehistoric races, and in Pliny's time the former was made, much as it is today, by heating wood in a pyramid covered with clay to exclude the air (*21*). According to the "Encyclopaedia Biblica," the word diamond as used in the old Testament probably does not refer to the true diamond but more likely to corundum (*22*), (*36*). The ancient Hindu scriptures, the Vedas, the Ramayana, and the Mahabharata, make frequent mention of the diamond. As early as 1704 Sir Isaac Newton stated in his "Optics" that it must be combustible, and in 1772 Lavoisier found this to be true (*23*). The English chemist, Smithson Tennant, proved in 1797 that it consists solely of carbon (*24*).

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II. ELEMENTS KNOWN TO THE ALCHEMISTS

The alchemists never succeeded in making gold from base metals, yet their experiments, recorded under a mystical and intentionally obscure terminology, gradually revealed metallic arsenic, antimony, and bismuth. Finally, in the latter part of the seventeenth century, the pale light of phosphorus began to illumine the dark secrets of alchemy and to disclose the steady advance of scientific chemistry.

. . . .

> "*. . . . Surely to alchemy this right is due, that it may be compared to the husbandman whereof Aesop makes the fable; that, when he died, told his sons that he had left unto them gold buried underground in his vineyard; and they digged over all the ground, and gold they found none; but by reason of their stirring and digging the mould about the roots of their vines, they had a great vintage the year following: so assuredly the search and stir to make gold hath brought to light a great number of good and fruitful inventions and experiments. . .*" (*1*)

The part played in ancient civilizations by gold, silver, copper, iron, lead, tin, mercury, carbon, and sulfur has already been shown. Certain other elements, although their lineage is not quite so ancient, have nevertheless had a history that extends far back through the centuries. In this group may be mentioned arsenic, antimony, bismuth, and phosphorus; and,

SIXTEENTH-CENTURY CARTOON ON ALCHEMY

strangely enough, these four simple substances have so many characteristics in common that they constitute one of the groups in the system of classification now universally used by chemists. Their early history is so shrouded in uncertainty that only in the case of phosphorus is it possible to assign the honor of discovery definitely to any person.

Arsenic

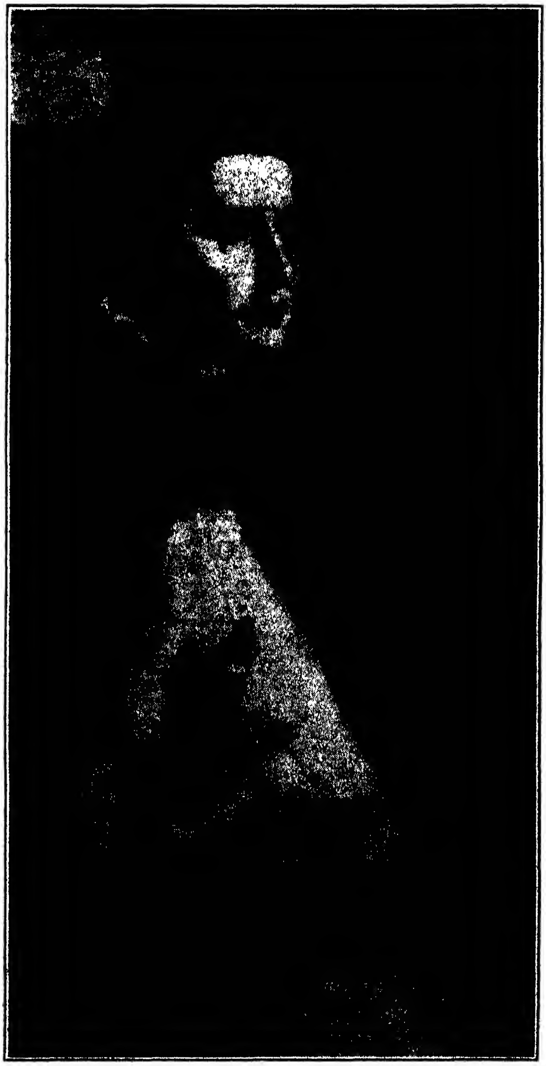
"For smelter fumes have I been named.
I am an evil, poisonous smoke...
But when from poison I am freed,
Through art and sleight of hand,
Then can I cure both man and beast,
From dire disease ofttimes direct them;
But prepare me correctly, and take great care
That you faithfully keep watchful guard over me;
For else am I poison, and poison remain,
That pierces the heart of many a one." (*36*)*

The so-called "arsenic" of the Greeks and Romans consisted of the poisonous sulfides, orpiment and sandarac, mined with heavy loss of life by slave labor (*2*). No one knows who first isolated the metal, but this honor is sometimes accredited to Albert the Great (Albertus Magnus, 1193–1280), who obtained it by heating orpiment with soap (*3*). Paracelsus (*15*), the eccentric and boastful medical alchemist of the sixteenth century, mentioned a process for obtaining metallic arsenic, "white like silver," by heating the so-called "arsenic" of the ancients with egg shells (*18*). Berthelot believed, however, that metallic arsenic was known much earlier than this, for it is easily reduced from its ores. Since it sublimes easily, and readily forms soft alloys with other metals, and since the arsenic sulfide, realgar, looks very much like the corresponding mercury ore, cinnabar, the alchemists regarded arsenic as a kind of quicksilver. The Pseudo-Democritus gave the following method of reducing the ore: "Fix the mercury obtained from arsenic (sulfide) or from sandarac, throw it on to copper and iron treated with sulfur, and the metal will become white" (*3*), (*17*), (*23*).

Signor Marcello Muccioli published in *Archeion* an article on the knowledge of arsenic possessed by the Chinese in about 1600, as exhibited in the Pen Ts'ao Kan-Mu (or Kang-mu), a 52-volume encyclopedia on

* *"Mein Nahme heisset Hütten-Rauch/*
Und bin ein gifftiger böser Schmauch...
Da aber Ich verlier den Gifft/
Durch Kunst und rechte Handgriff/
So kan Ich Menschen und Vieh curiren/
Auss böser Kranckheit offtmals führen/
Doch bereit mit recht/ und hab gut Acht/
Dass du haltst mit mir gute Wacht/
Sonst bin Ich Gifft und bleibe Gifft/
Das manchems Hertz im Leib absticht." (*36*)

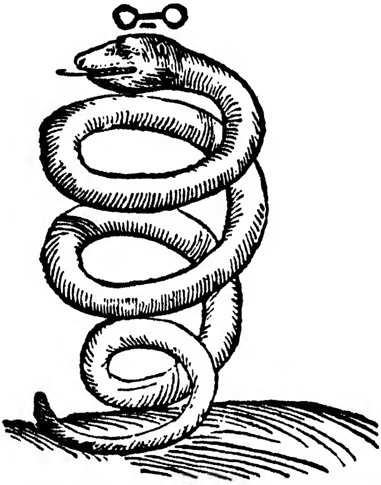
materia medica (*37*). Yoshio Mikami states that this work was printed in 1590 and that it was the result of thirty years of scholarly labor by its author, Li Shih-chen (*38*). The Chinese were thoroughly familiar with the poisonous properties of arsenic, and knew how to test whether or not a person had been poisoned by it. They used it to kill mice in their fields and insects in their rice plantations. Chinese persons were sometimes poisoned by drinking beverages which had stood for some time in new tin vessels. The author of the Pen Ts'ao attributed these cases to improper purification of tin prepared from minerals containing arsenic (*37*). After making erasures in their manuscripts (which were written on yellow paper), ancient Chinese scholars covered them neatly with a yellow varnish containing finely pulverized orpiment. Most of the orpiment was used by artists, however, as a pigment (*37*).



ALBERTUS MAGNUS, 1193–1280

German Dominican scholar and alchemist who interpreted Aristotle to the Latin races. Author of "*De Mineralibus*." He also contributed to mechanics, geography, and biology.

In 1649 Johann Schroeder published a pharmacopœia in which he gave two methods of obtaining metallic arsenic: (1) by decomposing orpiment, arsenious sulfide, with lime and (*2*) by reducing arsenious oxide with charcoal. The metallic nature of this element was thoroughly established through the researches of J. F. Henckel (1725), Georg Brandt (1733), (*21*), J. Browall (1744), and A. G. Monnet (1774) (*16*). Bishop Johan Browall also observed that it, like sulfur, is present, in small amounts at least, in most ores and that it sometimes occurs in the uncombined state (*3*), (*22*). J. H. Pott (1692–1777) and Browall (1706–1755) reduced white arsenic with soap (*22*).



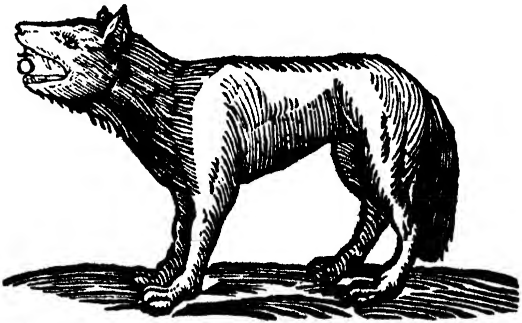
From Peters' "Aus pharmazeutischer Vorzeit in Bild und Wort"

SEVENTEENTH-CENTURY ALCHEMISTIC SYMBOL FOR ARSENIC

Antimony

> *"But antimony, like mercury, can best be compared to a round circle without end,...and the more one investigates it, by suitable means, the more one discovers in it and learns from it; it cannot be mastered, in short, by one person alone because of the shortness of human life."* (*58*)

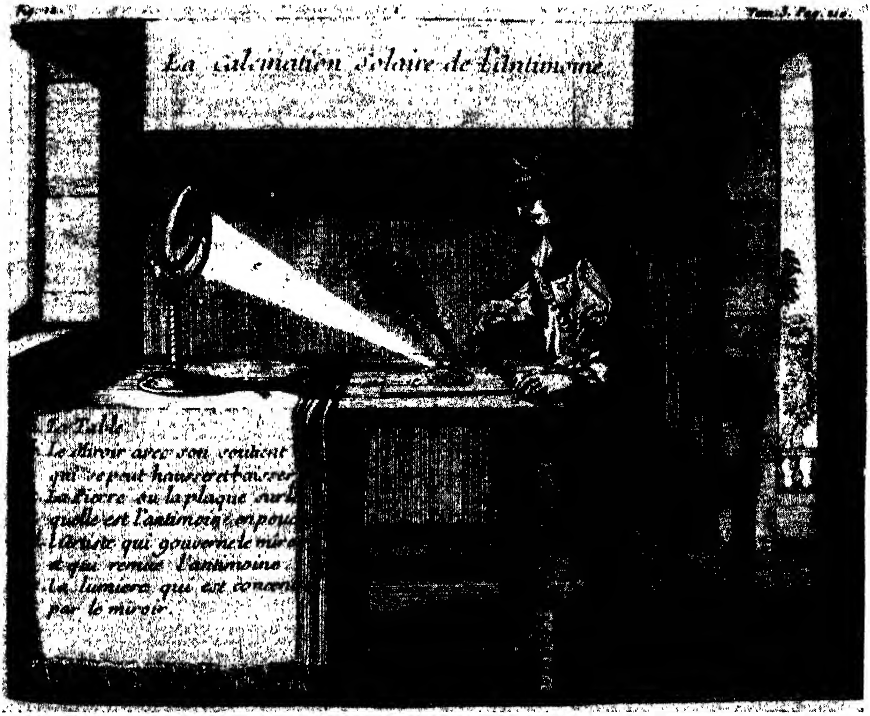
Antimony, like arsenic, was known to the ancients, but perhaps only in the form of its sulfide, which Oriental women of leisure used to use to darken and beautify their eyebrows (*4*). Berthelot's belief that metallic antimony was known to the ancient Chaldeans was based on his analysis of a most unusual vase that had been brought to the Louvre from the ruins of Tello, and which he found to consist of pure metallic antimony containing only a trace of iron (*5*), (*19*). He also quoted the following passage from Dioscorides: "One roasts this ore (antimonious sulfide) by placing it on charcoal and heating to incandescence; if one continues the roasting, it changes into lead" (*5*). Pliny issued the same warning in his description of the preparation of antimony medicinals, when he said: "But the main thing of all is to observe such a degree of nicety in heating it, as not to let it become lead" (*4*). Hence it is possible that the Greeks and Romans, like the Chaldeans, knew how to obtain antimony,



From Peters' "Aus pharmazeutischer Vorzeit in Bild und Wort"

SEVENTEENTH-CENTURY ALCHEMISTIC SYMBOL FOR ANTIMONY but since they did not have adequate methods of distinguishing between metals, they applied the indefinite term "lead" to all those that were soft, easily fusible, and black.

Georgius Agricola, in the sixteenth century A.D., was familiar with metallic antimony and an important use of it. "Stibium," said he in his "De natura fossilium," "when smelted in the crucible and refined, has as much right to be regarded as a proper metal as is accorded to lead by writers. If, when smelted, a certain portion be added to tin, a bookseller's alloy is produced from which the type is made that is used by those who print books on paper" (*39*).



From N. LeFevre's "Cours de Chymie," 1751

CALCINATION OF ANTIMONY

a, the table. *b*, the mirror, which can be raised or lowered. *c*, the stone or the slab, on which is placed the powdered antimony. *d*, the adept adjusting the mirror and moving the antimony. *e*, the light focused by the mirror.

The most famous of the early monographs on this element is the "Triumphal Chariot of Antimony," which first appeared in 1604, in German. Johann Thölde, operator of a salt-works in Frankenhausen, Thuringia, the editor of this work, claimed that it had been written by a fifteenth-century

Benedictine monk, Basilius Valentinus (*3*), (*6*). Since no conclusive evidence of the existence of this monk has been unearthed, and since the literary style of the "Triumphal Chariot" is much too modern for a fifteenth-century manuscript, many historians of chemistry have concluded that it must have been written in the latter part of the sixteenth century, possibly by Thölde himself. Felix Fritz, however, has concluded from comparison with the "Haligraphia" and other authentic publications of J. Thölde that he cannot have been the author of the "Triumphal Chariot" nor of the other writings attributed to Basilius (*40*).

BASILIUS VALENTINUS

Although the collection of chemical writings attributed to the fifteenth-century Benedictine monk, Basilius Valentinus, contains this alleged portrait, there is no conclusive evidence that such a person ever lived. Although the *Triumphal Chariot of Antimony* and other writings commonly attributed to him are much too modern for the fifteenth century, they are nevertheless of great historical value.

In 1707 Nicolas Lémery published his famous "Treatise on Antimony." He was born at Rouen on November 17, 1645. After studying pharmacy there under one of his relatives, he went to Paris in 1666 to complete his education. Dissatisfied with his progress under the unsociable but scholarly Christophe Glaser, demonstrator of chemistry at the Jardin du Roi, he resolved to tour France and learn first-hand from the greatest chemists of his day (*43*). Returning to Paris in 1672, he lectured to groups of students who rebelled against the prevailing ignorance and prejudice of the iatrochemists (*41*).

When M. Lémery had to choose between the two degrees, Doctor of Medicine or Master Apothecary, he selected the latter because of its closer relation to chemistry. B.-B. de Fontenelle described his public laboratory in the Rue Galande as "less a room than a cellar, and almost a magic cavern, illumined only by the light of the furnaces; yet the influx of people was so great that there was scarcely enough room for his operations. Even women, carried along by fashion, had the audacity to show themselves at such learned assemblies" (*41*).

Students came from all parts of Europe to live at his boarding school, "and the rooms of the quarter were filled with half-pensioners, who wished at least to eat at his home." His pharmaceutical preparations had a large sale, and the profits from his "bismuth magistery," a cosmetic, were sufficient for all the expenses of his household. In 1675 he published his famous "Cours de Chymie," which, unlike most scientific books, sold out edition after edition "like a work of romance or satire."

When Lémery was received into the Academy of Sciences in 1699, he decided to make a thorough analysis of the mineral known as antimony [stibnite] in a search for useful medicaments. After reading his paper in instalments to the Academy, he finally published it in 1707 as the "Treatise on Antimony." "When I resolved to study antimony thoroughly in all its aspects," said he, "I believed it proper to begin with some reflections on the nature of this compound and the places where it occurs; on the names which were applied to it, and their diversity; on how to select it; and on its medicinal virtues (*41*).

NICOLAS LÉMERY, M.D., 1645–1715

French chemist. Author of "*Cours de Caymie*," one of the textbooks that Scheele studied, and of a treatise on antimony.

"Antimony," said Lémery, "is a heavy, fragile, black, shining, odorless, insipid, and very sulfurous mineral crystallizing in laminae or in long needles. It occurs near the metals in many European mines, in Hungary, in Transylvania, in Brittany, in Poitou, and in Avernia. In Latin it is called *antimonium* or *stibium*. The alchemists, who abound in high-sounding names, have called it the *red lion* or *wolf*, because in the fire it devours the greater part of the metals; believing that many metals were derived from it, they have called it *the root of the metals;* because it receives various forms and colors, they have sometimes called it *Proteus;* sometimes *sacred lead*, or *philosophers' lead*, because they believed that, since this mineral devours many metals, it must be related to lead, which combines with many metallic substances (*41*).

"Among the merchants," continued Lémery, "we find two general species of antimony, the unworked mineral and the artificial: the former is taken from the mine loaded or mixed with many rock fragments, which the artisans call *gangue*.... This kind of antimony is not very common at the apothecaries' shops because it does not sell well....

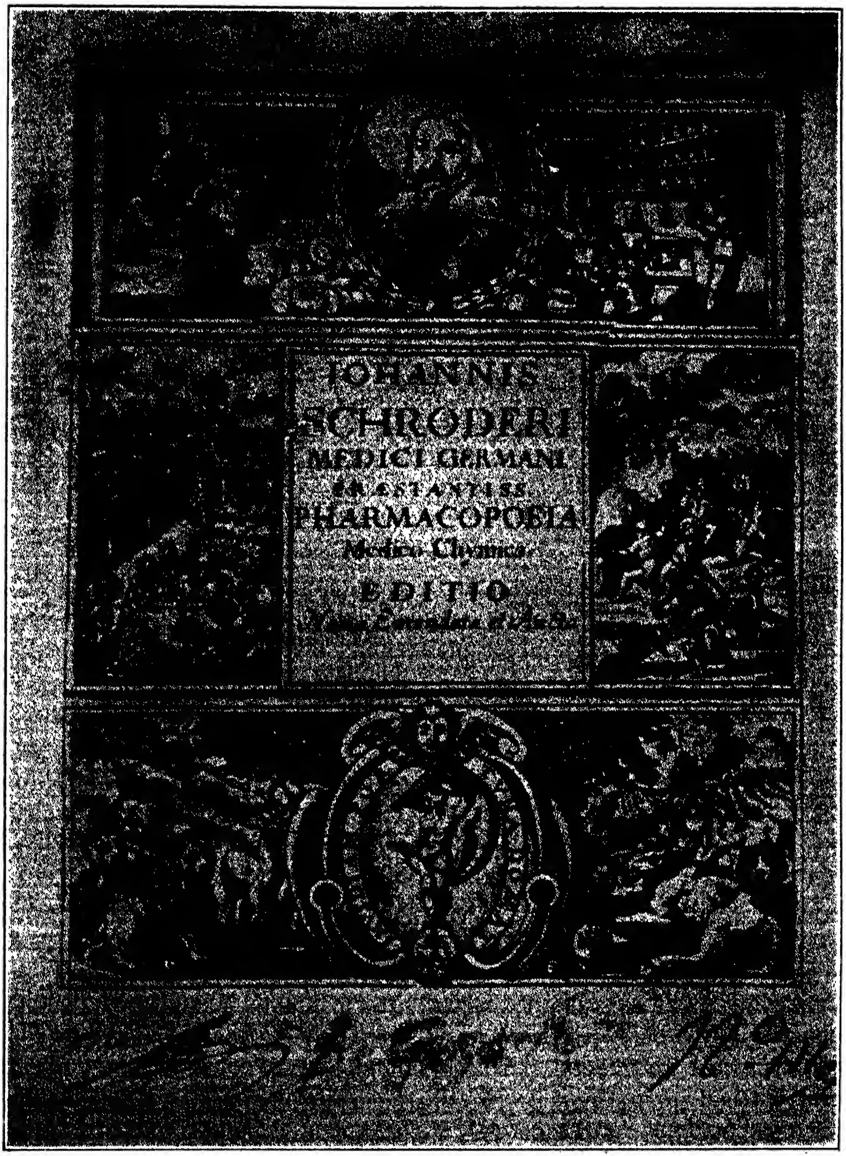
"The other kind of antimony," said Lémery, "is that commonly found at the apothecaries'; it is not different from the first except that it has been purified from its stony and earthy constituents. To purify it, the antimony taken from the mine is melted in vessels or crucibles in the fire, then removed by means of a perforated iron ladle to other vessels; the dirt which remains on the strainer is thrown away, and when the antimony has become cold, the vessels are broken open and removed, and it [the antimony] is sent to us in loaves as we see it. The antimony from Poitou is the handsomest and best, because most carefully purified...." (*41*). Before the discovery of stibnite in France, small specimens of it had been imported from Hungary.

By heating a mixture of crude, pulverized stibnite, saltpeter, and "red tartar" to redness in a crucible, Lémery obtained the metal, which fused completely, and condensed on cooling to form a massive, shining solid with the characteristic stellar structure of antimony on its surface (*41*). This highly specialized investigation led Fontenelle to foresee the great chemical monographs of today. "One might learn from this example," said he, "that the study of a single mixture is almost limitless and that each in particular might have its own chemist" (*41*).

Du Monstier, the editor of Nicolas Le Fevre's "Cours de Chymie," was more critical of Lémery's work. "A treatise that he published on antimony," said Du Monstier, "found itself exposed to the criticism of persons better informed than he on this mineral. I have been not a little surprised to see with what boldness he gives to sick persons antimony preparations which he devises and risks for the first time. One feels nevertheless on reading it that he has never seen those of Basil Valentine and of Suchten, both Germans whose works are held in high esteem by connoisseurs" (*42*).

Paul-Antoine Cap's biographical sketch of Lémery, written with the literary elegance of a French classic, opens with an imaginary word picture of Lémery entertaining in his laboratory his cosmopolitan friend Wilhelm Homberg. "At the end of the room, opposite the door," said Cap, "one noticed an immense furnace of solid and massive construction, surmounted by a basket full of instruments and various kinds of apparatus. Retorts and flasks there contended for space with matrasses, siphons, and aludels [earthen subliming pots]. Around this monumental furnace were placed other portable furnaces and polychrests, with their alembics, refrigerants, serpentines, rosaries, athanors, sand baths, and reverberatory furnaces, with their domes, their moor's head stills, and their copper or tin copings. In the center of this great room one saw a large table covered with utensils, urns, scorifiers, two-stage and three-stage glass alembics, and subliming apparatus with long cones arranged in pyramids. A copper lamp suspended from the ceiling swayed in the air, chemical symbols, arithmetical tables, slates streaked with chalk covered the walls of the room, and at each corner, hour-glasses of various sizes served for measuring time and regulating the duration of experiments.

"This laboratory," said Cap, "one could judge at a glance, was not that



From LaWall's "Four Thousand Years of Pharmacy"

FRONTISPIECE FROM JOHANN SCHROEDER'S PHARMACOPŒIA, 1646 of a sixteenth-century alchemist. One did not recognize here, by the peculiarity of their forms, the bizarre ideas conceived by these men on the nature of elements and mixtures. One saw none of those emblems, allegories, and symbolic figures with the aid of which they thought to hide from the knowledge of the common man their pretended secrets, already so obscure even for the true adepts. Nothing there suggested mystery, charlatanism, or occultism; on the contrary, everything bore the stamp of laborious study, of useful science; everything bespoke the modest scholar who devoted his life, in good faith and unreservedly, to the search for truth" (*44*).

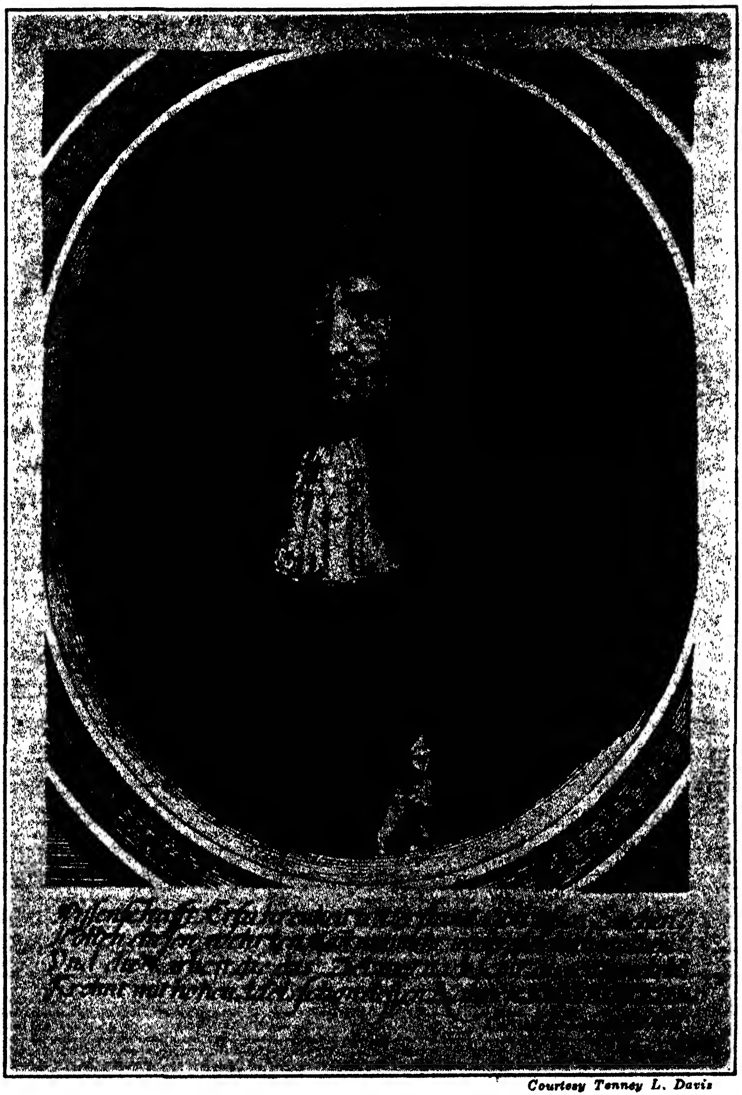
After the publication of his monograph on antimony, Lémery began to suffer from paralytic strokes and apoplexy, which on June 19, 1715, brought his life to a close. According to Fontenelle, "most of Europe learned chemistry from him, and most of the great chemists, French or foreign, have rendered homage to him by their learning. He was a man of unceasing industry, knowing only the bedside of his patients, his study, his laboratory, and the Academy, and showing that he who wastes no time has plenty of it" (*41*).

Bismuth

The Germanisches Museum in Nuremberg has a collection of boxes, caskets, chests, and little cupboards decorated in bright colors painted over a background of metallic bismuth (*28*), (*45*). In his "History of Bismuth from 1400 to 1800," the late E. O. von Lippmann stated that one of these was made in about 1480 (*46*). By 1572 this art had developed into a craft there, and in 1613 its artisans were incorporated into a guild (*47*). F. Wibel described a wooden casket in the Museum of Useful Arts at Hamburg, made in 1557. Over a chalk background attached with wax or glue, it has a metallic surface about one millimeter thick, overlaid with gold or amber lacquer. Investigation of this surface proved it to be bismuth. In the latter part of the eighteenth century, bismuth painting was superseded by a cheaper process in which perfected lacquers were applied directly to the wood (*47*).

In the middle of the fifteenth century the demand for bismuth increased. The early Gutenberg printing presses first used type cut from brass, and later, type cast from metals, such as lead, copper, or tin. In about 1450 a secret method of casting type from a bismuth alloy came into use (*46*). According to E. O. von Lippmann, the earliest mining publication to mention bismuth is that of Rülein von Kalbe, Burgomaster of Freiberg, who in 1505 referred to "Wysmudertz" as something already well known.

In his "Heaven of the Philosophers," Paracelsus (1493–1541) made a vague allusion to bismuth: "Two kinds of Antimony are found: one the common black, by which Sol [gold] is purified when liquefied therein.



Courtesy Tenney L. Davis

Johann Kunckel von Löwenstern, 1630–1702

German chemist, pharmacist, and glass technologist who gave an early account of phosphorus. Counselor of Metals under King Charles XI of Sweden.

(The portrait reproduced herewith is the frontispiece of Kunckel's "Ars Vitraria Experimentalis," published during his lifetime in 1679.)

This has the closest affinity with Saturn [lead]. The other kind is the white, which is also called Magnesia and Bismuth. It has great affinity with Jupiter [tin], and when mixed with the other Antimony it augments Luna [silver]" (*48*).

Georgius Agricola, a contemporary of Paracelsus, described the properties of bismuth in much greater detail and told how it was extracted from ores mined near Schneeberg in the Saxon-Bohemian Erzgebirge. In his book "Bermannus," Bermannus says to Naevius, "this which just now I said we called *bisemutum* cannot correctly be called *plumbum candidum* (tin) nor *nigrum* (lead), but is different from both and is a third one" (*49*). In believing it to be a specific metal, different from all others, Agricola was far in advance of his age, for the idea that bismuth was a kind of lead persisted even into the eighteenth century (*7*). The miners believed that there were three kinds of lead (ordinary lead, tin and bismuth) and that bismuth had progressed farthest in its transmutation into silver. When they struck a vein of bismuth they said naïvely and sadly, "Alas, we have come too soon" (*7*). Since they usually found silver below the bismuth, they called the latter "tectum argenti" or "roof of silver" (*24*).

In his "De re metallica" Agricola gave several methods of obtaining the metal by simple liquation of the native bismuth or by reduction with charcoal. Pulverized charcoal was placed in a small, dry pit, and a fire of beech wood was kindled over it. When the ore was thrown into the fire, the molten bismuth dripped out of it into the pit. The solidified cakes were later purified in a crucible (*24*).

After discussing the prevalent belief that the growth of precious stones and metals was governed by the stars, Padre Alvaro Alonso Barba stated in 1640 in his *Arte de los Metales:* "But this subordination and application is uncertain, as is also the conceit that Mettals are but seven in number, whereas it is very probable that in the bowels of the Earth there be more sorts than we yet know. A few years ago in the mountains of Sudnos in Bohemia was found a Mettal between Tin and Lead, and yet distinct from them both: there are but few that know of it, and 'tis very possible more Mettals also may have escaped the notice of the generality. And if one should admit the subordination and resemblance between Mettals and the Planets, modern experience, by excellent Teliscopes has discover'd that they are more than seven. Gallileo de Galiles [sic!] has written a Treatise of the Satelites of Jupiter, where one may find curious observations of the number and motion of those new Planets" (*50*).

Georgio Baglivi and Father José de Acosta believed that metals grew like plants under the influence of the planets. "Mettalls," said de Acosta, "are (as plants) hidden and buried in the bowels of the earth, which have some conformitie in themselves, in the forme and maner of their production; for that wee see and discover even in them branches and, as it were, a bodie, from whence they grow and proceede, which are the greater veines and the lesse...they are engendered in the bowels of the earth, by the vertue and force of the Sunne and other planets, and in long continuance of time they increase and multiply after the manner of plants...the rough and barren earth is as a substance and nutriment for mettalls and that which is fertile and better seasoned a nourishment for plants" (*51*).

In the fifth edition of his "Cours de Chymie," Nicolas Lémery confused bismuth with tin. "Bismuth," said he, "is a Sulphureous Marcassite that is found in the Tinn Mines; many do think it is an imperfect Tinn which partakes of good store of Arsenick; its pores are disposed in another manner than those of Tinn, which is evident enough because the Menstruum which dissolves Bismuth cannot intirely dissolve Tinn. There is another sort of Marcassite, called Zinch, that much resembles Bismuth.... Marcassite is nothing else but the excrement of a Metal, or an Earth impregnated with Metallick parts. The Pewterers do mix Bismuth and Zinch in their Tinn to make it found the better" (*52*).

In the eleventh edition of this work, Lémery said that older writers believed bismuth to be "a natural marcasite or an imperfect tin found in tin mines; but the moderns," said he, "believe with much likelihood that it is a regulus of tin prepared artificially by the English; my thought on this subject is that there is natural bismuth, but that it is rare, and that that which is commonly brought us from England is artificial. However that may be, it is certain that excellent bismuth is made with tin, tartar, and saltpetre; some also mix arsenic with it" (*53*).

Even as late as 1713 the *Memoirs of the French Academy* contained the statement that bismuth is composed of a mineral, crude sulfur, mercury, arsenic, and earth; and the pharmacopœias of that time contained recipes for making it (*7*). Lémery, for example, described the following method which he said was used in the English tin mines: "The workmen," said he, "mix this tin with equal parts of tartar and saltpetre. This mixture they throw by degrees into crucibles made red hot in a large fire. When this is melted, they pour it into greased iron mortars and let it cool. Afterward they separate the regulus at the bottom from the scoriæ and wash it well. This is the tin-glass which may be called the regulus of tin" (*13*). He thought that bismuth was "probably a regulus of tin prepared artificially in England in imitation of a rare natural bismuth" (*30*).

Caspar Neumann (1683–1737) clearly recognized bismuth as a specific metal (*31*). "Bismuth," said he, "is extracted from its own proper ore, which is found most plentifully in Saxony, near Schneeberg, and of which some quantities are met with also in Bohemia and in England. Many have affirmed that it is an artificial composition, and accordingly delivered processes for making it; of which processes I tried those which seemed to approach the nearest to probability. . . ." By heating "four ounces of

English Tin, two ounces of white Arsenic, one ounce of white Tartar, and half an ounce of Nitre, cemented and melted together" he obtained "a Regulus, weighing three ounces and three drams, so much resembling Bismuth as to be easily mistaken for it by one who had not thoroughly examined the appearance of that semi-metal. There are, however, some differences in the structure of the two. . . In their intrinsic properties they are extremely different: Thus the counterfeit, dissolved in Aqua fortis, forms a bluish coagulum, whilst the solution of the natural Bismuth continues uniform and limpid; the counterfeit, calcined and mixed with sulphur, exhibits nothing of that singular needled structure which the natural assumes in the same circumstances. Since therefore it has been reported that the Bismuth met with in the shops is an artificial production, and since experiment shows that it is capable of being imitated in its external form though not in its qualities, we ought to be upon our guard against such an imposition."

The French chemist Jean Hellot noticed that the tin smelters in Cornwall added natural bismuth, instead of the ingredients recommended in the pharmacopœias, to make the tin hard and brilliant, and in 1737 he obtained by fire assay of a cobalt-bismuth ore a button of the latter metal (*7*).

In 1753 Claude-François Geoffroy, a son of Claude-Joseph (Geoffroy the Younger), made a thorough investigation of bismuth (*7*), (*20*). Since this metal had not yet been introduced into medicine and was used only by pewterers for rendering tin whiter and more sonorous, it had been neglected by most chemists. J. H. Pott, however, had investigated it and published his "Exercitationes chymicae de Wismutho," and C.-F. Geoffroy first repeated the experiments of this famous German chemist. Although Pott had stated that bismuth loses $^3/_{38}$ of its weight when calcined in an open fire, Geoffroy found that the weight increased instead, and that, after the calx had once been formed, no amount of heat caused any further increase.

Knowing that lead behaved similarly, Geoffroy sought for other points of resemblance between the two metals. Although it had long been assumed that lead was the only metal suitable for the cupellation of silver and gold, an artist had informed Charles-François de Cisternay du Fay in 1727 that, if the gold contained certain impurities such as emery it was necessary to cupel it with a large quantity of bismuth. Pott and Geoffroy both found that bismuth can also be used in the cupellation of silver. Although Pott had stated that bismuth is not combustible, Geoffroy saw it burn with its characteristic blue flame (*54*). He found ten points of similarity between bismuth and lead but nevertheless distinguished clearly between them and closed with the words "In a second Memoir I shall ascertain whether or not this analogy holds on treating these two substances with acids and different salts" (*54*). Because of his premature death in 1753, C.-F. Geoffroy was unable to complete this second memoir.

In his "Elements of the Art of Assaying Metals," Johann Andreas Cramer pointed out the close association of bismuth with arsenic and cobalt. "Every ore of Bismuth," said he, "as is shewn by the chemical analysis, is reduced to the State of Ore by Arsenick: For this goes out of it by Sublimation. You find in the same Ore that Kind of Earth that gives an azure Colour to Glasses, of which we have already spoken in the Article of Cobalt. Whence it is evident that the Ore of Bismuth may without Impropriety be called Cobalt of Bismuth: The more, because you will find in any ore of Bismuth the same Principles as in Cobalt, only in a different Proportion" (*55*). This close association of bismuth and cobalt in nature made it difficult for early chemists to distinguish between them (*56*).

THE ALCHEMIST, BY D. TENIERS (1610–1690)

In Cromwell Mortimer's notes to the second English edition of Cramer's work there is a description of an ore sent from Cornwall which was "so very rich of Bismuth that, by only holding a Piece with a Pair of Tongs against a clear Fire, the melting Bismuth will run down as soon and as easy as cheese will drop in toasting" (*55*).

When the Swedish mineralogist J. J. Ferber visited Derbyshire in the latter part of the eighteenth century, he found that "Mineralogy in England is still in its cradle, and it is not long since the Cornish miners threw away the bizmuth with the refuse, as a substance perfectly useless; and they would have remained in the same error had it not been for Dr. Schlosser of Amsterdam" (*57*).

Phosphorus*

In the seventeenth century there lived in Hamburg a merchant by the name of Hennig Brand (or Brandt), who was apparently the first man ever to discover an element. Of course, gold and lead and the other metals and non-metals used in ancient civilizations must have been discovered by somebody, but these great contributors to human knowledge are as unknown today as is that greatest of all inventors—the man who made the first wheel.

Brand was a soldier in his youth, and it is said that later he became "an uncouth physician who knew not a word of Latin" (*8*). In spite of this deficiency he married a wealthy wife, who honored him for his scientific attainments. While endeavoring to improve his financial standing, he was lured by the spell of alchemy to search for the King of Metals. No one knows what led this zealous alchemist to hope that in human urine he might find a liquid capable of converting silver into gold, but it is well known that his queer experiments made in 1669 produced results that were both startling and strangely beautiful. Small wonder that he was delighted with the white, waxy substance that glowed so charmingly in his dark laboratory. The method of obtaining this light-giving element, which is now called phosphorus, Brand kept secret, but the news of the amazing discovery soon spread throughout Germany (*9*).

There lived at that time a famous chemist, Johann Kunckel (1630–1702). a son of an alchemist in the court of the Duke of Holstein (*10*). The younger Kunckel studied pharmacy, glass-making, and assaying; worked in the Dresden laboratory of John George II, Elector of Saxony; taught chemistry in the famous medical school at Wittenberg; and later managed the glass-works in Berlin belonging to Frederick William, the Elector of Brandenburg. His last years were spent in the service of King Charles XI of Sweden, who conferred on him the titles, Baron von Löwenstern and Counselor of Metals (*10*).

One day Kunckel proudly exhibited to a friend in Hamburg—much as a modern chemist might show a specimen of hafnium or rhenium—a phosphorescent substance. To his great surprise, the friend had not only seen this substance before, but offered to take Kunckel to the home of the medical alchemist, Dr. Brand, to see a still more remarkable substance that shines spontaneously in the dark. Brand, they found, had given away his entire supply, but he took Kunckel to the home of a friend to see the wondrous element.

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* See also "The Supplementary Note on the Discovery of Phosphorus," Part III, pp. 41–57.

Kunckel, in the heat of excitement, wrote immediately to his friend, Dr. Johann Daniel Krafft of Dresden. The latter, however, proved to be a false friend, for, without replying to Kunckel's letter, he went immediately to Hamburg and bought the secret from Brand for two hundred thalers. Just as the transaction was being made, Kunckel arrived on the scene. All his attempts to learn the secret process failed, but he did find out that the new luminous substance, which had come to be known as phosphorus, had been obtained from urine (*8*).

Kunckel then began experimenting with this fluid, and was finally successful. Like Brand, he refused to reveal the method, giving as his reason the fear that dangerous accidents with phosphorus might become frequent. According to Homberg, Kunckel's process was essentially as follows: Fresh urine was evaporated nearly to dryness, after which the black residue was allowed to putrefy in a cellar for several months. This material was heated, gently at first and then strongly, with twice its weight of sand, in a retort leading to a receiver containing water. After the volatile and oily constituents had distilled over, the phosphorus began to settle out in the receiver as a white, waxy solid. This was the part of the process which Kunckel thought too dangerous to reveal to the public. To prevent fires and explosions, it was necessary to remove the flame as soon as the phosphorus began to appear, and to keep the receiver closed until it became cold (*8*).

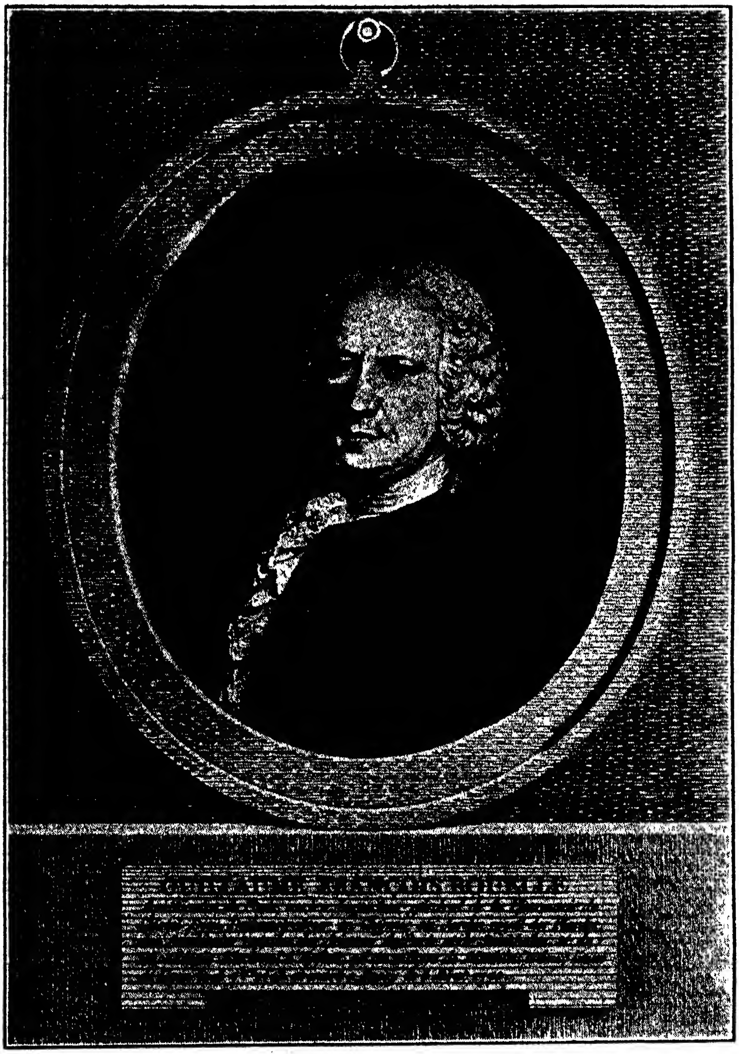
ROBERT BOYLE, 1627–1691

English chemist and physicist famous for his researches on gases, his air pump, his early experiments on the mechanical origin of heat, and his independent discovery of phosphorus. One of the founders of quantitative analysis.

Kunckel not only prepared phosphorus, but also cast it in molds to obtain the stick phosphorus now familiar to all chemistry students. He also introduced its use as a medicinal, and his famous book on the subject bears the curious title: "Treatise of the Phosphorus Mirabilis, and Its Wonderful Shining Pills" (*10*). It is pleasant to know that his phosphorus researches were not without reward, for Duke Johann Friedrich of Hanover paid him an annual pension for the rest of his life (*9*). According to Thomas Thomson (*11*), William Homberg purchased Kunckel's secret of making phosphorus by giving in exchange the ingenious barometer invented by Otto von Guericke, in which a little man comes to the door of his house in dry weather and discreetly retires within as soon as the air becomes moist (*35*).

It would be unfair to conclude this brief account of the discovery of phosphorus without mentioning that Robert Boyle, the illustrious English pioneer in pneumatic chemistry, also discovered it independently. He prepared it by a method somewhat resembling that of Kunckel, but, as Boyle himself said, without any previous knowledge of that process. Boyle was a man of such high integrity that one cannot doubt the truth of his statement. Krafft claimed, however, to have communicated his process directly to Boyle (*32*). Boyle's assistant, Godfrey Hanckwitz, made phosphorus on quite a large scale, and exported it to Europe (*12*). One of his advertisements reads as follows: "Ambrose Godfrey Hanckwitz, chemist in London, Southampton Street, Covent Garden, continues faithfully to prepare all sorts of remedies, chemical and galenical . . . . For the information of the curious, he is the only one in London who makes inflammable phosphorus, black phosphorus, and that made with acid, oil, and other varieties. All unadulterated. . . Solid phosphorus, wholesale 50s. an ounce, and retail, £3 sterling, the ounce" (*14*).

In 1737 a stranger in Paris offered to sell the secret process of making phosphorus to the Academy of Sciences. After accepting the offer, the French government appointed Jean Hellot chairman of a committee to study the process, and his detailed report, published in the Memoirs of the Academy for 1737 and later in P.-H. Macquer's textbook of chemistry, made the process accessible to all chemists (*12*), (*34*). The *Dictionnaire de Chymie* published in Yverdon, Switzerland, in 1767 states that "as this process, up to the present, has been more curious than useful, and as, moreover, it is both costly and embarrassing, I have no knowledge whatever that any chemist repeated it then in France except M. Rouelle, who, shortly thereafter, opened his course in chemistry, in which he tried to make phosphorus in presence of his audience. I was present at his first attempt; M. Hellot, who took great interest in this experiment, came also, and followed the process throughout its entire duration. We spent the night there; this first operation failed, to tell the truth, because of a defect in the retort; but in the following years M. Rouelle succeeded a number of times in making phosphorus in his course" (*29*), (*31*). However, phosphorus is no longer prepared by the unpleasant method described above. In 1769 the Swedish scientists Scheele and Gahn (*33*) found that it is an important constituent of bones, and in the following year Scheele succeeded in isolating it from them (*8*), (*25*), (*26*), (*27*). It really is strange that phosphorus was discovered so early in the history of chemistry, for the reactions involved in Brand's method are rather complex, and even today this element is not isolated with ease.



Courtesy Tenney L. Davis

Guillaume-François Rouelle
1703–1770

Parisian apothecary. Former inspector-general of the pharmacy at the City Hospital. Demonstrator in chemistry at the Royal Botanical Garden. Member of the Royal Academies of Science of Paris and Stockholm and of the Electoral Academy of Erfurt. Born in the village of Mathieu two leagues from Caen September 16, 1703, died at Passy Aug. 3, 1770. (Translated from the French caption on the frame.)

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III. SUPPLEMENTARY NOTE ON THE DISCOVERY OF PHOSPHORUS*

Although most accounts of the discovery of phosphorus are based mainly on the writings of Kunckel von Löwenstern and record the events essentially as they have just been described, other early records present a somewhat different story. In 1902 Hermann Peters, a famous German historian of chemistry and pharmacy, made a thorough study of the autograph letters of Brand, Krafft, Kunckel, Homberg, G. W. Leibniz, and others which are preserved in the Royal Library at Hanover, and found that, although the various accounts differ in many respects, they all agree on one point: namely, that phosphorus was originally discovered by Dr. Hennig Brand of Hamburg. Although most historical records present Dr. Brand as an almost mythical character and do not even mention his Christian name, he emerges from these rare old letters as a real human being.

. . . . . .

In his correspondence with the Abbé Nollet, Raimondo di Sangro (1710–1771) mentioned the "perpetual lamps" of Saint Augustine (354–430), which were sometimes found in sepulchers of the early Christians. Raimondo di Sangro believed that these lamps contained phosphorus, and Gino Testi considered this obscure point in chemical history worthy of further investigation (*26*), (*27*).

In his "History of the match industry" in the JOURNAL OF CHEMICAL EDUCATION, M. F. Crass, Jr., quoted Paracelsus' recipe for "the separation of the elements from watery substances" (*28*), (*29*). Paracelsus' "icicles which are the element of fire," which he apparently obtained by distillation of urine, may possibly have been elemental phosphorus. If that be the case, it is difficult to understand why they aroused so little interest.

Most authorities agree that the original discoverer of elemental phosphorus was the seventeenth-century alchemist and physician Hennig (or Henning) Brand of Hamburg. Gottfried Wilhelm Leibniz (1646–1716) was personally acquainted with Brand, corresponded with him regularly for at least four years, and wrote a history of the discovery of phosphorus. According to this great philosopher and mathematician, Brand was living in 1677 at the Michaelisplatz in Hamburg, in the newer part of the city. His wife, Frau Margaretha Brand, was proud of his attainments, and the dates of her letters show that she lived to enjoy the honors which resulted from his epoch-making discovery. A stepson often assisted the doctor in his experiments, and there were other children as well. Although Dr. Brand was something of a spendthrift and borrower, the family must have lived comfortably on their income of 1000 *Reichsthalers* a year. Visionary

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* Readers who prefer a shorter, yet connected, account of the discovery of the elements may omit chapters III, VI, VIII, X, XII, XIII, and XVI.

Courtesy Fisher Scientific Co.

The artist who painted this scene, Joseph Wright of Derby (1734–97), called it "The Alchymist in search of the philosopher's stone discovers phosphorus and prays for the successful conclusion of his operation, as was the custom of the ancient chymical astrologers." It was first exhibited in 1771, and was engraved by William Pether in 1775.

and impractical though he was, his skill in chemistry won the respect of his contemporaries at a time when iatrochemistry held the forefront in medical thought. Ambrose Godfrey Hanckwitz once referred to him as "old honest Brandt of Hamburg" (*15*).

When his alchemical experiments revealed the beautiful light-giving element, Brand called it *cold fire* ("*kaltes Feuer*"), or, affectionately, "*mein Feuer.*" The luminous substance which Kunckel subsequently exhibited in Hamburg was "Balduin's phosphorus," a phosphorescent calcium nitrate which had been prepared by distilling a solution of chalk in nitric acid (*2*), (*3*), (*20*). Brand's "cold fire" interested Kunckel greatly, and when he wrote about it to his friend, Johann Daniel Krafft (or Kraft) of Dresden, the latter also came to Hamburg. They visited Brand and suggested that they might be able to sell his secret to some royal personage for a high price. According to Leibniz, both Kunckel and Krafft learned the secret directly from Dr. Brand at that time (*1*), (*4*).

The learned Dr. Krafft soon made the new substance known far beyond the walls of Hamburg as he traveled to the Netherlands, to England, and even to northern America ("*dem mitternächtlichen Amerika*") (*4*). In an attempt to sell the secret process, he exhibited the *cold fire* in the court of the Great Elector, Friedrich Wilhelm of Brandenburg. On April 24, 1676, at nine in the evening, all the candles were extinguished while Dr. Krafft performed before a large assembly a number of experiments with the "perpetual fire." However, he did not reveal the method by which it had been prepared.

AMBROSE GODFREY

According to Ince (Ref. *15*) this represents Ambrose Godfrey Hanckwitz, but according to Pilcher (Ref. *22*) it is Hanckwitz's son, Ambrose Godfrey (1685–1756). Since the portrait was made from life in 1738 it must represent the son.

In the following spring Dr. Krafft went to the court at Hanover, where G. W. Leibniz was serving as librarian and historian under Duke Johann Friedrich, and exhibited two little phials that shone like glowworms. When Leibniz suggested that a large piece of phosphorus might give enough light to illumine an entire room, Dr. Krafft told him that this would be impractical because the process of preparation was too difficult (*1*). On September 15, 1677, Krafft performed some startling experiments with it before Robert Boyle and several other members of the Royal Society. At the request of Robert Hooke, Boyle wrote a detailed report of them. After the candles had been removed to another room and "the windows closed with wooden-shuts," Krafft's precious little specimen of phosphorus, of the size of two peas, was seen to shine brightly. When Krafft scattered tiny bits of it on the carpet, Boyle was delighted "to see how vividly they shined . . . And these twinkling sparks, without doing any harm (that we took notice of) to the Turky Carpet they lay on, continued to shine for a good while . . . Mr. Kraft [sic] also calling for a sheet of Paper and taking some of his stuff upon the tip of his finger, writ in large characters . . . DOMINI, . . . which . . . shone so briskly and lookt so oddly, that the sight was extreamly pleasing, having in it a mixture of strangeness, beauty, and frightfulness . . ." (*23*). One hundred and fifty-seven letters from Krafft are still preserved in the library at Hanover.

Courtesy Mathematics Dept., The University of Kansas

GOTTFRIED WILHELM LEIBNIZ
1646–1716

German mathematician, philosopher, historian, and scientist. Independent discoverer of the differential calculus. He was personally acquainted with Brand and Krafft, and wrote a detailed account of the discovery of phosphorus, including biographical sketches of Brand, Krafft, Kunckel, and Becher.

In July, 1678, Leibniz went to Hamburg and drew up a contract between Duke Johann Friedrich and Dr. Hennig Brand according to which the latter was to correspond regularly with Leibniz and keep him informed about new developments regarding the "*cold fire.*" The Duke's part of the contract consisted in the promise to pay ten thalers a month, with the stipulation that sixty thalers, or six months' allowance, would be paid in advance for revealing the secret processes ("*bei Communicirung der Composition und ander bereit habender Curiositäten*") (*1*).

Shortly after this Dr. J. J. Becher went to Hamburg and attempted to engage Brand for the Duke of Mecklenburg-Güstrow. In this, however, he was intercepted by Leibniz, who took Dr. Brand back with him to Hanover and advised Duke Johann Friedrich that it would be best to keep him at the court or send him to the Harz Mountains until the secret processes had been tested. Leibniz thought that Dr. Brand would be able to prepare a large quantity of phosphorus in the mountains and that he might perhaps find the philosophers' stone. Brand did not go to the Harz, however, but remained in Hanover for five weeks, preparing a fresh supply of phosphorus outside the city and showing Leibniz the secret process according to the agreement. The latter also prepared a quantity of phosphorus and sent some of it to the physicist Christian Huygens in Paris, who was studying the nature of light (*1*), (*5*). Thus Leibniz was the fourth person to prepare the new element (Brand, Krafft, Kunckel, Leibniz) (*1*).

Brand, however, was highly dissatisfied with the pay he had received, and wrote angry letters to Leibniz claiming that it was insufficient for his traveling expenses and the care of his family at home. Frau Margaretha Brand also wrote angrily to Leibniz, and her husband berated Krafft for inducing him to place confidence in Leibniz instead of in Dr. Becher. He also accused Krafft of having received one thousand thalers for the phosphorus in England.

On December 24, 1678, Dr. Krafft sent this letter to Leibniz, saying, "Since you mention having received an angry letter from him [Brand], I am sending you mine herewith. You may compare them and see which is the prettier" (*1*). Nevertheless, Leibniz advised the Duke to deal more liberally with Dr. Brand, partly out of sympathy, and partly to prevent him from selling his secrets to others.

This tactfulness calmed Brand's wrath, and in 1679 he planned another trip to Hanover to prepare phosphorus on a large scale and reveal his other chemical secrets. A weekly salary of ten thalers in addition to board and traveling expenses was agreed upon, and a later letter shows that, on this second trip, Brand worked for Duke Johann Friedrich two months. The last letter from Brand in the Hanover library is dated August 23, 1682, but, according to Leibniz, he was still living ten years later (*1*), (*4*). Hermann Peters thought that possibly other letters from Brand may still exist in Hamburg or elsewhere.

Leibniz communicated Brand's method of making phosphorus to Count Ehrenfried Walter von Tschirnhaus (1651–1708) in Paris, and sent him a specimen by request. When Tschirnhaus published the Brand-Leibniz recipe in the history of the Royal Academy, Colbert recommended him for membership in the French Academy of Sciences, and on July 22, 1682, he was elected. According to Dr. Peters, this recipe was also published in the fifth edition of Nicolas Lémery's "*Cours de Chymie*" in 1683 (*1*).

When Krafft went to England, he exhibited phosphorus in the court of Charles II and showed it to the Honorable Robert Boyle (*1*), (*4*), (*6*), (*23*). The great English scientist then prepared it by a slightly different method and studied its properties more thoroughly than did any other chemist of the seventeenth century (*1*).

When Wilhelm Homberg defended Kunckel's claim to the re-discovery of phosphorus after the original secret process had been lost to the world, Leibniz strove to defend the rights of Dr. Brand and stated emphatically that the real discoverer of phosphorus was still living long after Krafft and Kunckel had made the element known, and that he used to complain bitterly about his false treatment (*1*). Although Krafft published his recipe in 1679, Brand was still living in 1692, and even by 1710 Leibniz had heard no report of his death. A. Godfrey Hanckwitz once paid the following tribute to the great Hamburg chemist:

> . . . as all things have their period so has also the *vitalis lucula* (scintilla, spark) by approaching age. By (in the case of) this urosophus Brandt, it daily lessened and wore off, till at last in the midst of his best experiments it e'en quite extinguished. His fine stare fire, which through art he produced, remained for his memory longer with us than himself. . . . and shined longer than his *flammula vitae,* that in time of his best occupation did turn and return to its fiery sphere. His acquaintances and confidents would feign (if wishes would have done it) have retarded his decrease to set it farther off. . . (*15*).

Robert Hooke and his contemporaries, recalling the animal origin of phosphorus, had several "disputes, whether there were any such thing as *flammula vitae:* and it was conceived by some that the experiments of phosphorous [sic] plainly proved such a *flammula* as being extracted either immediately out of the blood or mediately out of the urine" (*30*).

According to Leibniz, Brand was not secretive, but, on the contrary, gave over the process too readily to Krafft and Kunckel in return for some little gifts and the promise of larger payments (*1*), (*4*). When Kunckel tried out the process at home, his first attempts were unsuccessful. His complaining letters to Brand brought him no further information, however, for the Hamburg chemist had soon regretted his poor bargain. In the meantime Kunckel experimented by a trial-and-error method, and, since he had seen the process and was familiar with Brand's distillation apparatus, he finally succeeded in correcting his own mistake. He then had the audacity to claim the discovery for himself (*1*), (*4*).

In a letter to Brand written from Wittenberg on June 25, 1676, Kunckel asked him directly for the details of preparation, suggesting that the recipe might be worded so obscurely as to be meaningless to others, and assuring him that there would be no danger of any one else opening the letter. He complained because Brand had given some phosphorus to Krafft and the chaplain of the Pest House, and begged him to give no more of it to any one else. Kunckel modified the Brand process a little by adding sand to the urine before distilling. In June, 1676, he told his friend, G. C. Kirchmaier, professor of chemistry at Wittenberg, about the new process, and the latter published a paper on it. Whether Kunckel ever prepared the new element on a large scale or not is not known, but at the end of his history of phosphorus he wrote, "However, I am not making it any more, for much harm can come of it" (*2*), (*3*).

Dr. Hermann Peters concluded from a study of these old letters that Kunckel did not re-discover phosphorus, but merely made a little of it by Brand's method, and that, even without Kunckel, phosphorus would have remained known to the world through the efforts of Krafft, Leibniz, and Boyle (*1*).

In 1726 W. Derham published a book entitled "*Philosophical experiments and observations of the late eminent Dr. Robert Hooke, F.R.S. and Geom. Prof. Gresh and other eminent Virtuoso's in his time,*" in which he included a detailed description of Brand's process of making phosphorus (*20*). Under the title "Phosphoros Elementaris, by Dr. Brandt of Hamburgh," Derham wrote:

"Take a Quantity of Urine (not less for one Experiment than 50 or 60 Pails full); let it lie steeping in one or more Tubs, . . .till it putrify and breed Worms, as it will do in 14 or 15 Days. Then, in a large Kettle, set some of it to boil on a strong Fire, and, as it consumes and evaporates, pour in more, and so on, till, at last, the whole Quantity be reduced to a Paste. . . and this may be done in two or three Days, if the Fire be well tended, but else it may be doing a Fortnight or more. Then take the said Paste, or Coal; powder it, and add thereto some fair Water, about 15 Fingers high. . .; and boil them together for $^1/_4$ of an Hour. Then strain the Liquor and all through a Woollen Cloth. . .the Liquor that passes must be taken and boil'd till it come to a Salt, which it will be in a few Hours. Then take off the Caput Mortuum (which you have at any Apothecary's, being the Remainder of Aqua Fortis from Vitriol and Salt of Niter) and add a Pound thereof to half a Pound of the said Salt, both of them being first finely pulverized. And then for 24 Hours steep'd in the most rectify'd Spirit of Wine, two or three Fingers high, so as it will become a Kind of Pap.

Then evaporate all in warm Sand, and there will remain a red, or reddish, Salt. Take this Salt, put it into a Retort, and, for the first Hour, begin with a small Fire; more the next, a greater the 3d, and more the 4th; and then continue it, as high as you can, for 24 Hours. Sometimes, by the Force of the Fire, 24 Hours proves enough; for when you see the Recipient white, and shining with the Fire, and that there are no more Flashes, or, as it were, Blasts of Wind, coming from Time to Time from the Retort, then the Work is finished. And you may, with Feather, gather the Fire together, or scrape it off with a Knife, where it sticks."

Derham said of this phosphorus, "I saw some of it, press'd with a Quill that was cut, and it fired Gun-powder about it. Mr. Concle [Kunckel?] writ also with it on Paper, and the Letters all shined in the Dark. . .My Author says he had once wrapp'd up a Knob in Wax, at Hanover, and it being in his Pocket, and he busy near the Fire, the very Heat set it in

AMBROSE GODFREY HANCKWITZ
1660–1741

In this portrait by George Vertue (1718), the bust of Hanckwitz is shown surrounded by his apparatus. At the left are shown the furnace and receiver used in the manufacture of phosphorus. The molten product was removed with a ladle to the molds in which it was cast into sticks, the entire operation being carried out under water. Flaming phosphorus and the phoenix, emblem of fire and immortality, figure prominently in the foreground.

Flame, and burn'd all his Cloaths, and his Fingers also; for though he rubbed them in the Dirt, nothing would quench it, unless he had had Water; he was ill for 15 Days, and the Skin came off. . ."

The following incident related by Nicolas Lémery illustrates the carelessness of early chemists in handling this dangerously flammable element. "After some Experiments," said he, "made one day at my house upon the Phosphorus, a little piece of it being left negligently upon the Table in my Chamber, the maid making the bed took it up in the bed-clothes she had put upon the Table, not seeing the little piece: the person who lay afterwards in the bed, waking at night . . . , perceived that the coverlid was on fire" (*31*).

In his article entitled "The Aerial Noctiluca," Robert Boyle mentioned that "the experienced chymist Mr. Daniel Krafft had, in a visit that he purposely made me, shewn me and some of my friends, both his liquid and consistent phosphorus. . ." In return for some information about "uncommon mercuries, . . . he [Krafft], in requital, confest to me at parting, that at least the principal matter of his phosphorus's was somewhat that belonged to the body of man. . ." (*6*), (*19*). On September 30, 1680, Boyle's efforts to prepare the luminous element were crowned with success, and two weeks later he deposited his recipe with the secretaries of the Royal Society, who, however, did not open it until after he had died in 1691 (*7*).

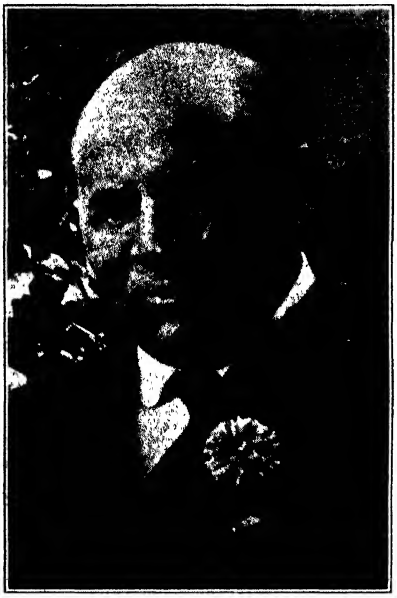
Boyle's assistant, A. G. Hanckwitz or Hanckewitz (1660–1741), was therefore able to develop the process on a commercial scale, improve it, and export phosphorus to the continent (*8*), (*9*), (*17*). Hanckwitz had been brought over from Germany at an early age by his honored master. He later built furnaces and stills in Maiden Lane, and traveled through the Netherlands, France, Italy, and Germany. He founded a famous pharmaceutical firm in London, and so great was his fame that a letter once came to him safely from Berlin addressed simply, "For Mr. Godfrey, famous Chymist in London" (*15*). He was known in England simply by the name Ambrose Godfrey, the German surname being reserved for formal occasions.

The letters which constitute his correspondence with Sir Hans Sloane from 1721 to 1733 are still preserved in the British Museum (*18*), and in 1858 Joseph Ince wrote an interesting biographical sketch of Hanckwitz based on correspondence, diaries, and notes (*15*). According to Caspar Neumann, "Mr. Godfrey himself. . .was once in danger of his life from [phosphorus], his hand being burnt so terribly that for a time he was out of his senses, and for three days lay in exquisite pain, as if his hand had been constantly in a fire" (*21*). In spite of all his dangerous experiments, this great disciple of Robert Boyle lived to be an octogenarian. He died on January 15, 1741, and was survived by three sons, Boyle, Ambrose, and John Godfrey, all of whom shared their father's interest in science.

Hanckwitz kept his recipe for phosphorus a profound secret, and, even in the article which he published in 1733, forty or fifty years after leaving Boyle's laboratory, gave only an obscure description of the process (*8*), (*10*). The sons evidently adopted the same policy, for one of them wrote:

> As to the phosphorus made of urine called Kunckel's, we have it described by the Honourable Mr. Boyle, Mons. Homberg, and others. But I shall beg to be excused for not discovering the process how I prepare it, or from giving any farther light into its production than what was done by my father, before the Royal Society, in the year 1733 (*16*).

Yet only two years after this obscure and vague description of the process was published, the aged Hanckwitz allowed Dr. J. H. Hampe, the court physician, to coax him into revealing the secret (*8*). Not many years ago the late Dr. Max Speter found this long-lost recipe in an unexpected place. In the published correspondence of the Counselor of Mines, Johann Friedrich Henckel (or Henkel) of Freiberg (1679–1744), there appears a letter from Dr. Hampe written in London on August 29, 1735 (*8*), (*11*). In reply to Henckel's inquiries regarding Hanckwitz and the secret process, Dr. Hampe wrote that Boyle's famous assistant was still living, but so forgetful because of advanced age that little could be learned from him. Nevertheless, through diligent questioning of the old man, he had succeeded in getting the essential details of the phosphorus recipe which Henckel had requested. Dr. Hampe asked Henckel to write him about any difficulties that might arise in his attempts to make phosphorus, in order that the aged Hanckwitz might be further questioned if necessary.



MAX SPETER, 1883–1942

Transylvanian inventor and historian of chemistry. Author of many articles on Boerhaave, Geoffroy the Elder, Marggraf, Black, and Lavoisier. Contributor to "*Das Buch der grossen Chemiker.*" In 1929 he found the Boyle-Hanckwitz recipe for phosphorus, after it had been kept secret for more than two centuries (*25*).

From this letter it appears that "the true key" to the process, which consisted in distilling a mixture of solid and liquid excrement, "was, above all else, that everything be done under water; especially while pouring it into the molds and while cutting it, enough water must always be at hand" (*8*), (*11*). To avoid the necessity of redistillation, or rectification, Hanckwitz pressed the phosphorus through leather, being careful to keep it under water. In a second letter written on September 9 of the same year, Dr. Hampe gave Henckel further information about the process. On November 15 he asked Henckel not to divulge the secret to any one else and suggested that they keep each other informed about the experiments with phosphorus (*8*).

From Ferchl's Apotheker-Kalender for 1932

JOHANN HEINRICH LINCK*
1675–1735

Leipzig apothecary who communicated Kunckel's method of preparing phosphorus to J. F. Henckel. The "Golden Lion" pharmacy was in possession of the Linck family for three generations, and their museum of natural history and art was known throughout all Germany.

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* Courtesy Mr. Arthur Nemayer, Buchdruckerei und Verlag, Mittenwald, Bavaria.

Henckel had learned the details of Kunckel's method of preparing it as early as 1731 from Johann Linck, an apothecary in Leipzig. In his letter of May 29, 1731, Linck stated that a better method was being used in England by Hanckwitz, but that he did not know the details (*8*), (*11*).

Hanckwitz, however, like his contemporaries, had entirely incorrect views as to the chemical nature of phosphorus. "Its principal Contexture," said he, "is found to consist of a subtile Acid concentrated by the Salt of Urine, and of a fat depurated Oil. . .The Phlogistic Part is so slightly connected with the other Principles, that the least Motion, Friction, or Warmth, sets it on fire. . .Phosphorus may be called an urinous Soap, as it consists of the saline and oleaginous Parts of the Urine. . .In regard to the Parts whereof Phosphorus consists, it may be considered as the Soot of a deflagrated Oil; and so may every combustible Substance be looked upon as a Kind of Phosphorus, as consisting of inflammable Materials. . .Phosphorus is more immediately compounded of a Salt tending to the Nature of Sal Ammoniac, of an urinous Salt, of an Acid, and an oily Phlogiston, with a subtile Earth. . ." He also stated that glowworms "seem to have Phosphorus lodged in their Bodies." Hanckwitz claimed that Kunckel, Krafft, and Brand had been able to obtain only "unctuous and opaque" phosphorus, whereas his was "hard, transparent, and glacial" (*10*).

Another of the early experimenters with phosphorus was the Abbé Nollet, who watched Jean Hellot and others demonstrate its properties before the French Academy of Sciences in 1737 (*32*). The procedure was described in detail in the Memoirs of the Academy of Sciences for that year and later in P.-J. Macquer's "Elements of the Theory and Practice of Chymistry." Even in the eighteenth century, chemists had a completely erroneous idea of its nature. "Almost all the Chymists," said Macquer, "consider Phosphorus as a substance consisting of the Acid of Sea-Salt combined with the Phlogiston, in the same manner as Sulphur consists of the Vitriolic Acid combined with the Phlogiston" (*33*). This conception was based, according to Macquer, on the presence of salt and phlogiston (carbonaceous matter?) in the urine from which phosphorus is prepared and on the fact that phosphoric acid, like hydrochloric, throws down a precipitate with silver nitrate (*33*).

In 1743 A. S. Marggraf, a student of Henckel, found a much better way of preparing this element from urine (*12*), (*13*), (*14*), (*24*) and, since the phosphorus business was no longer as profitable as it had been, he promptly published the process. According to Marggraf, the new method had been suggested by Henckel's statement that, when the "calx of lead" was digested with sal ammoniac, potassium carbonate, and old urine, and then distilled, a good grade of phosphorus could be obtained. According to Mielcke, the microcosmic salt, $NaNH_4HPO_4 \cdot 4H_2O$, in the urine was converted by heating into sodium metaphosphate, $NaPO_3$. In the meantime the potassium carbonate and carbon reduced the lead chloride and lead oxychloride to lead, after which the carbon and lead reduced the sodium metaphosphate to sodium pyrophosphate and phosphorus (*12*). Dr. Speter also studied the correspondence between Marggraf and Henckel regarding this interesting method of preparing phosphorus.

Marggraf tried in vain to prepare phosphorus without urine. When he used mixtures of various chlorides with "vegetable coals, and even animal matters such as oil of hartshorn, human blood, etc.," all his attempts failed. When he separated some microcosmic salt from urine, however, mixed the salt with lampblack, and distilled the mixture, "he obtained from it a considerable quantity of very fine phosphorus . . . , whence he concluded that in this Saline matter resides the true Acid that is fit to enter into the composition of phosphorus" (*33*).

In 1688 Bernhard Albinus (Weiss) mentioned the presence of phosphorus in the ash of mustard and cress (*34*). In 1743 Marggraf prepared it from wheat and mustard (*35*). "In order to demonstrate by experiment," said he, "that the vegetables we enjoy every day or occasionally also contain that which is necessary for the production of the phosphorus, I found in Albinus' Dissertation on Phosphorus as well as on page 477 of the celebrated Hofmann's [Friedrich Hoffmann's] notes to Poterius that the seeds of black and white mustard and of cress yield phosphorus. Since I myself, however, still had no experience with it, yet found in Professor Pott's Collegio Mscpto on the first edition of Boerhaave's Chemistry that wheat, rye, and other similar grains yield phosphorus, I made the following experiments . . ." (*35*).

When Marggraf distilled the seeds of white and black mustard, garden cress, pepper, and wheat, he obtained phosphorus from each of them except the pepper. Although Albinus had added sand, Marggraf found this to be unnecessary. For the sake of economy, Marggraf used pepper from which the essential oil had previously been distilled (*35*). When he found that microcosmic salt could be reduced to phosphorus, he became curious to know the source of this salt in human urine. Since he found higher concentrations of microcosmic salt and phosphoric acid in the urine in the summer (when people eat more garden products such as mustard and cress), he thought it probable that these might be the source of the microcosmic salt (*36*). Although the modern chemist has simple qualitative tests for phosphates, Marggraf and his contemporaries were obliged to carry out the much more difficult process of liberating elemental phosphorus in order to detect its presence.

Since plants and animals are able to concentrate phosphorus in their tissues, and since these tissues contain their own reducing agents, E. B. R. Prideaux does not consider it surprising that physicians and pharmacists of the seventeenth and eighteenth centuries first prepared this element from substances of vegetable and animal origin (*36*).

Lavoisier said that "Phosphorus is met with in almost all animal substances and in some plants which, according to chemical analysis, have an animal nature .... The discovery that M. Hassenfratz has made of this substance in wood charcoal would make one suspect that it is commoner in the vegetable realm than has been thought; this much is certain: that, when properly treated, entire families of plants yield it" (*37*). Apothecary J. K. F Meyer of Stettin wrote in 1784 that he had observed, several years previously, a permanent green color in the essences he prepared by digesting green herbs in copper vessels. He concluded that phosphates in the leaves had reacted with the copper to form copper phosphate (*38*).

William Lewis stated in 1759 that the ash of bones and horn resembles chalk and "the earth of the shells of sea-fishes . . . in being easily soluble in the nitrous [nitric], marine, and vegetable acids, and not in the vitriolic." The only difference he was able to observe between the calcareous earth from shells and the bone ash was that the latter is "not changeable by fire into Lime: How strongly soever the earth of Bones and Horns be calcined, it continues insipid and gives no manifest impregnation to water" (*39*).

When J. G. Wallerius analyzed eggs, bone, and other animal substances in 1760, he detected lime, and had a vague idea that they also contain certain other earths. In a footnote to this paper in the *Neues chemisches Archiv*, Crell stated, "Hr. W. did not yet know the nature of the animal earth which the unforgettable Scheele made known to us: that is, that it consists of lime and phosphoric acid" (*40*). In 1769 C. W. Scheele and J. G. Gahn discovered that phosphorus is an important constituent of bone. Although some historians of chemistry have attributed this discovery to Gahn or Scheele alone, the late Dr. Max Speter proved from Gahn's own notes that both had a part in it (*41*).

Courtesy Edgar Fahs Smith Memorial Collection

JOHAN GOTTSCHALK WALLERIUS
1709–1785

Swedish chemist, physician, mineralogist, and agriculturist. T. Bergman's predecessor as professor of chemistry, metallurgy, and pharmacy at Upsala. In his analyses of bone and other animal substances in 1760, he detected the calcium but not the phosphorus.

In his *Chemisches Journal* Lorenz von Crell mentioned a rare publication announcing this discovery. "In the medical commentaries of a society of physicians at Edinburgh I found in the first issue of the third part (p. 97 *ff*. of the German translation, Altenb. 1776) a report by Hrn. D. Heinrich Gahn of Stockholm of how one can obtain a phosphorus from the bones of animals and especially from the hartshorn. I searched for a more detailed account of this wonderful discovery of Herr Gahn's. Except for the remark in C. W. Scheele's investigation of fluorspar that it has recently been discovered that *the earth in bones or horns is lime saturated with phosphoric acid*, all my searching was in vain. In the meantime, since this process of working up bones to obtain the phosphorus seemed to me to belong to the masterpieces of chemical decomposition, I repeated the experiment according to the instructions in the aforementioned book, and, to my great pleasure, found it to be true" (*42*). The "Heinrich Gahn" mentioned by von Crell was probably J. G. Gahn's brother, Henrik Gahn, assessor in the medical school.

Even to J. G. Gahn and Scheele, phosphorus was a rarity. When Scheele first read the English translation of his treatise "On air and fire," he found that Johann Reinhold Forster had translated the word *Gran* as *ounces* instead of *grains*. "Nine ounces of phosphorus," said Scheele, "I have never yet seen" (*43*).

Gahn was a man of broad interests who "often laid aside the *Philosophical Transactions* or his blow-pipe to read aloud, near the sewing-table in the next room, now a poem by Kellgren, Franzén, Fru Lenngren, Leopold, or Voltaire, now a comedy by Molière or Holberg; or to exhibit a little mechanical or optical masterpiece; or to study the instruments for some household art and present a method of improving them" (*44*).

During the preparations for his daughter Margareta's wedding, Gahn and his family witnessed a most unusual manifestation of household chemistry. Since the recipe for salting ham with a brine containing sugar and saltpeter had been lost, Fru Gahn trusted to her memory, and made the mistake of adding altogether too much saltpeter and too little water. On the wedding day, when the ham was being boiled in the brine, the terrified, breathless housekeeper came running in to report that the ham had burst into flame and was throwing out flashes of lightning, and that the house was in danger of burning down. The ensuing scene was described by Gahn himself in a letter written to Berzelius on September 20, 1807: "It was really a peculiar and pretty sight: first there rose, over the entire surface of the water in the kettle, bright, flashing sparks, which silently appeared and disappeared; then long and sometimes brilliant and violent streams of flashes were thrown in all directions over the water" (*45*). "After the kettle had been removed from the fire and left to cool," said Gahn, "I could see that the shining particles were originally small oil-like drops, several of which I quickly caught, and picked up, and found to be actually *phosphorus!*" (*45*).

The kind assistance of the late Dr. Max Speter of Berlin, who graciously contributed a number of important references on the early history of phosphorus, is gratefully acknowledged.

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IV. SOME EIGHTEENTH-CENTURY METALS

Among the metals isolated in the eighteenth century may be mentioned zinc, cobalt, nickel, and manganese, the last three of which were discovered in Sweden. The researches of Marggraf, Georg Brandt, Cronstedt, and Gahn which led to the recognition and isolation of these elements were scientific contributions of the first rank, and the personalities of these great men are well worthy of study and emulation. Other metals of this period will be discussed in later chapters.

. . . . . .

> "*Knowing how contented, free and joyful is life in the realms of science, one fervently wishes that many would enter their portals.*" (*1*).

Zinc

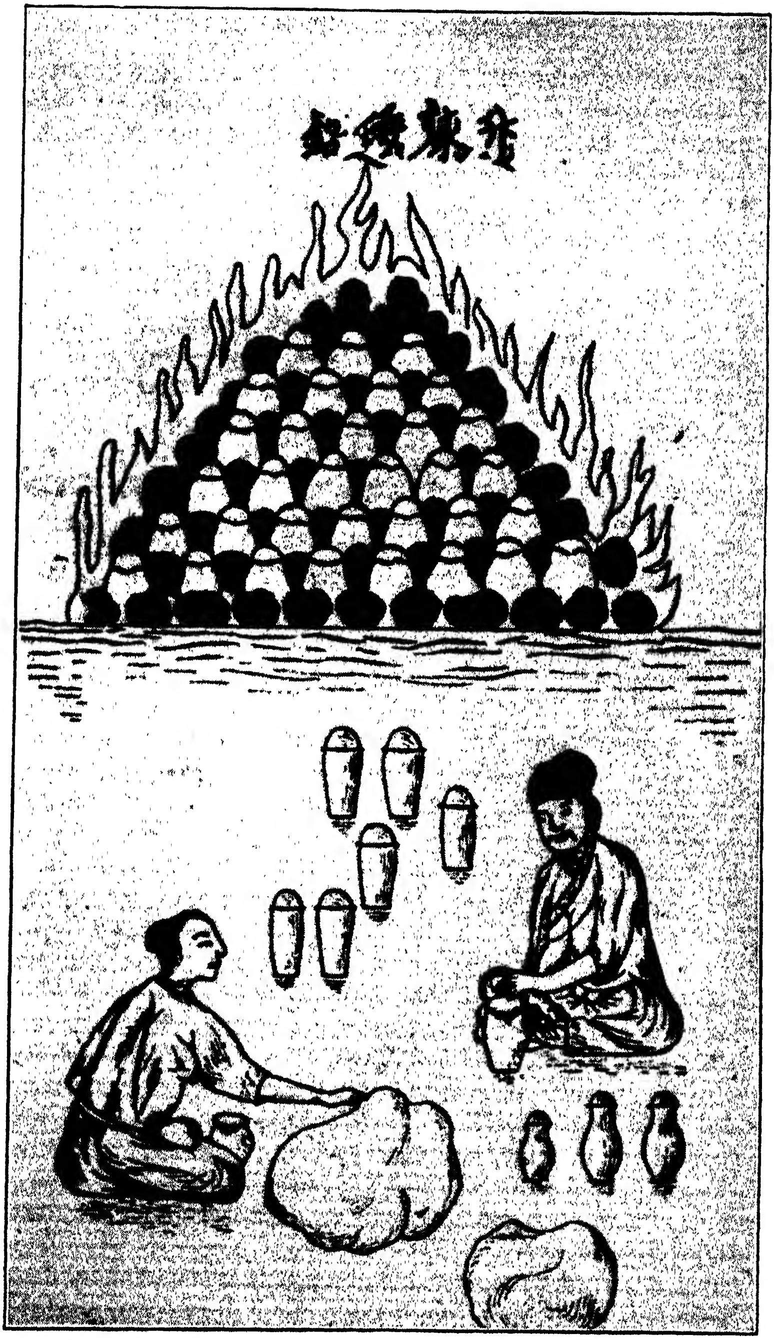
Pliny the Elder and Dioscorides of Anazarbus mentioned that zinc compounds were used for healing wounds and sore eyes (*41*), (*42*). In the latter part of the thirteenth century A.D., Marco Polo described the manufacture of zinc oxide in Persia: "Kubenan is a large town. The people worship Mahommet. There is much iron and steel . . . . They also prepare both *Tutia* (a thing very good for the eyes) and *Spodium;* and I will tell you the process. They have a vein of a certain earth which has the required quality, and this they put into a great flaming furnace, whilst over the furnace there is an iron grating. The smoke and moisture, expelled from the earth of which I speak, adhere to the iron grating, and thus form *Tutia*, whilst the slag that is left after burning is the *Spodium*" (*43*).

From Bugge's "Das Buch der grossen Chemiker"

ANDREAS SIGISMUND MARGGRAF
1709–1782

German chemist who distinguished between potash and soda, realized that clay contains the peculiar oxide now known as alumina, recognized magnesia, isolated zinc from calamine, and discovered sugar in the beet.

Centuries before zinc was discovered in the metallic form, its ores were used for making brass. Ancient metallurgists probably lost this volatile metal as vapor because their apparatus was not designed for condensing it. The late E. O. von Lippmann, a great authority on the history of science, searched the writings of Aristotle, Pliny, and Dioscorides in vain for any mention of it, but an idol con-



Z. Angew. Chem., 1912

Production of Zinc in China as pictured in the Chinese technical lexicon "Tien kong kai ou."

taining 87.5% of that metal was found in a prehistoric Dacian ruin at Dordosch, Transylvania (*2*). P. C. Râу states that the Hindu king, Madanapâla, recognized zinc as a metal as early as 1374 (*3*), and it is probable that the art of smelting the ores originated in India and was carried first to China. A Chinese book entitled "Tien kong kai ou" printed in 1637 describes the metallurgy and uses of this metal (*2*), (*44*).

A hundred years before zinc was smelted in Europe, it was being sold there by Portuguese traders who brought it from the Orient (*4*). G. Agricola mentioned the formation of "zincum" in the furnaces in Silesia (*31*). Small amounts of metallic zinc were obtained as a by-product of the lead industry at Goslar, Prussia, and G. E. Löhneyss described the process as follows: "The metal *zinc* or *counterfeht* is formed under the smelting furnaces and in the crevices of the wall where the bricks are not well plastered. When the wall is scraped, the metal falls down into a trough placed to receive it. The metal is not much valued, and the workmen collect it only when they are promised Trinkgeld" (*2*), (*18*), (*28*).

Caspar Neumann (1683–1737) gave the following first-hand description of the Goslar zinc works: "The greatest quantities of Zinc come from the East Indies, in large oblong pieces; and from Goslar, commonly in round cakes or loaves. Of the origin of the East-India Zinc we have no certain account: The Goslarian is extracted from the Lead- and Silver-ores of Rammelsberg by a particular contrivance in the structure of the furnace. The Zinc, naturally contained in the ore, separates during the fusion from the other metallic matters, being elevated by the heat in form of fume, which passes into a reservoir made for that purpose in the front wall, over the gutter by which the Lead runs off. The reservoir for the Zinc is inclosed, on the inside, by a large flat stone, only some chinks being left for the fumes to enter; and on the outside, by another stone, which is closely luted, and frequently sprinkled during the process with cold water, to cool and condense the fumes. Each smelting lasts twenty hours, beginning at ten in the forenoon and ending at six next morning. When the fusion of the ore is completed, the workman dextrously strikes the outer stone of the reservoir with an Iron rod, so as to loosen some of the luting at the bottom; upon which the Zinc, collected during the process, runs out like Quicksilver. He continues to tap till nothing more will run; then melts the Zinc again in an iron pot, and casts it into hemispherical masses. I have several times been at this work, and kept at it two days and a night together without leaving the furnace.

"Though a part of the Zinc is thus obtained in its metallic form, a part is also dissipated, and a very considerable one adheres to the sides of the furnace in the form of a calx. . . The produce of Zinc is extremely variable. . . At Goslar, when the due precautions happen to be neglected, there is not so much Zinc detained as to be worth collecting. . . " (*33*).

Johann Kunckel and Georg Ernst Stahl believed that the ore calamine contained a metal that alloys with copper to form brass, and even as late as 1735, the Swedish chemist Georg Brandt thought that calamine could not be reduced to a metal except in presence of copper (*2*), (*19*). During the years between 1768 and 1781, Richard Watson, Bishop of Llandaff, published his famous chemical essays (*45*). In the one on zinc, he quoted the following passage from page 295 of the French translation of J. F. Henckel's (or Henkel's) "Pyritologia": "One makes, for example, with the calamine, not only iron (in small amounts, to be sure), but also a very large quantity of zinc, which one obtains not only on presenting to it the substance with which it can incorporate itself (that is to say, copper, which is its lodestone), but also this half-metal shows itself simply on addition of a fatty substance which metallizes; it is only necessary to avoid letting this phoenix be reduced to ash, to keep it from burning, and to observe the time and circumstances" (*46*). Henckel prepared metallic zinc by reduction of calamine, but kept the process secret (*29*), (*47*). As the shining metal came forth from the hard, lusterless ore, he was reminded of the Egyptian symbol of immortality, the phoenix, a fabulous bird which rose to new life from its ashes.

Courtesy Virginia Bartow

RICHARD WATSON, BISHOP OF LLANDAFF
1737–1816

Professor of chemistry, and later professor of divinity, at Cambridge. Between 1768 and 1781 he published a collection of chemical essays on water, air, coal, lead, zinc, salt, saltpeter, and other common substances. He gave an excellent account of the early history of zinc.

In the introduction to his German translation of P. M. de Respour's "Special Experiments on the Mineral Spirit," Henckel mentioned in 1743 that "In our smelting furnaces at Freyberg we have obtained the essence of zinc [zinckische Wesen] in power but not in form" (*48*). He believed that their failure to obtain "corporal" [metallic] zinc must have been due to the complex nature of their ore, to the construction of their furnaces, and to the long-continued heating, which made it "impossible for the phoenix, even when resurrected from its ash, to withstand the fire" (*48*).

"Nevertheless," said Henckel, "zinc is a metal with regard to its consistency, luster, specific gravity, tenacity, and mercurial fluidity in the fire, but also not a metal with respect to its flammability and complete combustibility, wherein it is entirely different from all other metals" (*48*).

The Flemish metallurgist P. M. de Respour published the first edition of his "Special Experiments on the Mineral Spirit" in 1668, when he was twenty-four years old. He prepared a minute amount of metallic zinc by gently heating a mixture of zinc oxide and fat on a sandbath for six or seven days. When he subsequently distilled this mixture, he found in the retort only a little gray, fuming deposit in which he was unable to distinguish any metallic particles. When he rubbed it with mercury, however, and distilled off the latter, he obtained a little metallic zinc (*48*).

Bishop Watson stated that, "though Henckel was the first, Dr. Isaac Lawson was, probably, the second person in Europe who procured zinc from calamine .... Our English writers ... speak in high terms of Lawson ..." (*46*). Since the Bishop prefaces his description of the metal with the words "If the reader has never seen a piece of zinc," it must have been a rarity even in the second half of the eighteenth century (*46*).

When Lawson observed that the flowers of *lapis calaminaris* were the same as those of zinc and that they had the same effect on copper, he worked tirelessly until he found a method of separating the zinc from this mineral. He never realized any profit, however, from this discovery (*46*).

While in Leyden, Dr. Lawson belonged to a scientific club presided over by the great Swedish botanist Carl von Linné, and became so engrossed in making mineralogical analyses that he gave up attending lectures. Another of Lawson's Leyden contemporaries who held him in high esteem was Dr. Hermann Boerhaave (*49*), (*50*).

Johann Andreas Cramer assisted Dr. Lawson for several years in his chemical experiments in Leyden. In the preface to the second English edition of Cramer's "Elements of the Art of Assaying Metals," there is a fine tribute to Dr. Lawson, who "had resided much longer at Leyden than those foreigners usually do who go there to qualify themselves for the Practice of Physick. He then employed himself in the Cultivation of those arts which he had there been taught; particularly of Chemistry; and was highly esteemed for his Skill therein, and lived in great Intimacy with Boerhaave . . . and with several other Men of great Learning, who resided in that University . . . as also with Linnaeus . . . Doctor Lawson afterwards served as Physician to the British Army in Flanders; where, by his Death, in the year 1745, the World was deprived of the Advantage of many useful Discoveries. To him we owe several of the Observations contained in this Work . . . " (*51*).

In a great research "On the method of extracting zinc from its true mineral, calamine," A. S. Marggraf in 1746 reduced calamine from Poland, England, Breslau, and Hungary with carbon in closed retorts, and obtained metallic zinc from all of them (*2*), (*19*), (*27*). He found the ore from Holywell to be especially rich in it. He stated that both J. H. Pott and J. H. Henckel had known how to prepare this metal and keep it from burning.

Marggraf also showed that the lead ores of Rammelsberg contained zinc and that zinc can be prepared from blende, or sphalerite (*53*). "Who would think," said he, "that this furnace calamine [in Saxony] is derived from blende and that this blende contains the zinc earth, for I know of no one who ever thought of it except the aforementioned Herr Professor Pott, who mentioned on page 119 of his treatise on pseudo-galena that pulverized blende, melted with carbon and copper, did not, to be sure, entirely convert the copper to brass, yet made it rather yellow, and therefore correctly concluded that it must contain an earth related to calamine. Still less has anyone, so far as I know, ever yet made known the process of actually preparing zinc from this mineral, which, however, I hope to make clear from the following experiment" (*53*).

Marggraf was probably unaware that in 1742 Anton von Swab, a stepbrother of Emanuel Swedenborg, had distilled zinc from calamine at Vestervik, Dalecarlia, and that, two years later, he had even prepared it from blende (*18*). Since the vapors rose to the top of the alembic before passing into the receiver, this process was called distillation *per ascensum*. In the fall of 1752 Swab and A. F. Cronstedt developed at government expense the use of Swedish zinc ores in the manufacture of brass, to avoid the necessity of importing calamine. They installed equipment near Skisshyttan for the washing, slow oxidation, decomposition, and calcination of the ore and for distillation of the zinc. Swab showed that blende can be reduced even in the absence of copper (*52*). In 1755 Cronstedt's share in the work was taken over by Sven Rinman (*32*), (*46*), (*47*). Rinman so improved the metallurgical process that zinc could be smelted not merely in the form of grains or powder, which required subsequent melting and consequent loss of metal, but also in fluid form directly from the ore (*81*).

Even in the early nineteenth century, the value of sphalerite was not appreciated. In Henry R. Schoolcraft's report on the lead mines of Missouri, which was published in the *American Journal of Science* for 1821, appears the statement: "Zinc is abundant, but as the ore is the sulphuret, it is not very valuable. It is not mentioned that the calamine, which is *the useful* ore of zinc, has been found" (*54*).

Some Swedish Metals

In the eighteenth century Sweden outstripped all other countries in the discovery of new elements. It is blessed with a rich supply of rare ores and, moreover, it had a long succession of brilliant chemists and mineralogists whose greatest delight was to investigate these curious minerals. In the century following the accidental discovery of phosphorus, three new metals, cobalt, nickel, and manganese, were discovered by Swedish chemists.

Cobalt

"Thus with Hermetic art the Adept combines
The Royal acid with cobaltic mines;
Marks with quick pen, in lines unseen portrayed,
The blushing mead, green dell, and dusky glade;
Shades with pellucid clouds the tintless field,
And all the future Group exists conceal'd;
Till waked by fire the dawning tablet glows,
Green springs the herb, the purple floret blows,
Hills, vales, and woods in bright succession rise,
And all the living landscape charms the eyes" (*62*).

Analyses of blue glass made by the ancients show that the earliest specimens were colored sometimes with cobalt but much more often with copper (*64*), (*65*), (*66*). In the tomb of Tut-ankh-Amen were many specimens of dark blue glass, only one of which was found to contain cobalt (*67*).

Paracelsus, in his "Book of Minerals," which forms part of the 1658 Latin folio edition of his works, gave only a vague description of cobalt (*7*). The unknown author of the writings attributed to "Basil Valentine" stated in his treatise "On the great stone of the ancient philosophers" that "Among the minerals are included all metals, ores, marcasite, cobalt (Kobold), talc, zinc, shining pyrites, and stones" (*63*). Berthelot thought, however, that metallic cobalt must have been prepared before the thirteenth century, for the alchemists understood how to roast and reduce ores. They did not, however, know how to refine the metals and distinguish between them (*7*).

Near the end of the fifteenth century, a troublesome and supposedly worthless mineral, "cobalt," was found in large quantity in the mines on the borders of Saxony and Bohemia (*68*). The miners disliked it because of the labor of removing it and also because the arsenic in it injured their health. The first glassmaker who really understood the specific ability of these ores to impart a blue color to glass was Christoph Schürer of Platten, Bohemia, who, in about the middle of the sixteenth century, prepared a blue color for pottery at the Eulen smelter in Neudeck (*69*). On a visit to Schneeberg he collected some pieces of the ore. When he tested them in his glass-furnace, he found that they fused with the vitreous mass and yielded a handsome blue glass. At his plant in Neudeck he prepared the new color, first for the use of local potters and later for shipment to Nuremberg and thence to the Netherlands, where the skilled glass-painters understood better how to use it (*68*).

Courtesy Tenney L. Davis

BERNARD PALISSY
1510?–1589

French glassmaker, surveyor, potter, agriculturist, and chemist who was familiar with "zaffer," or cobalt blue.

"Who is it in the suburbs here,
This Potter, working with such cheer, . . .
This madman, as the people say,
Who breaks his tables and his chairs
To feed his furnace fires . . .
O Palissy! within thy breast
Burned the hot fever of unrest" (*82*).

The poorer grades were used for making bluing and blue starch for laundry (*70*). Roasted cobalt ore was soon exported in casks to eight color-mills in the Netherlands. When the people of Schneeberg began to remark that the part of the cobalt ore which dropped down while being roasted contained more color than the roasted ore itself, Elector Johann Georg subsidized the development of an extensive cobalt industry there (*68*). A mixture of roasted cobalt ore and sand, which was added to conceal its nature, was known as *Zaffer*, *Safflor*, or *Safran*. Most of the cobalt ores in the Erzgebirge also contained bismuth, which was easily separated by liquation.

After mentioning calamine, Vannoccio Biringuccio stated in his "Pirotechnia" in 1540: "Another similar half-mineral is *Zaffer*. It is heavy like metal. It does not melt by itself, but when mixed with vitreous substances it becomes like water and colors them blue. Zaffer is therefore used for coloring glasses blue or for painting glass vessels with a blue color. At the artist's desire, it also serves as a black pigment in these crafts, by taking more of it than is permissible for blue" (*71*).

The great sixteenth-century French ceramist Bernard Palissy once wrote: "I know no plant nor mineral nor any substance which can tinge stones blue or azure except saphre, which is a mineral earth, extracted from gold, silver, and copper, which has very little color, except gray inclining a little toward the violet. Whenever the said saphre is incorporated with vitreous substances, it makes a marvelously fine azure: hence one may know that all stones having an azure color have taken their tint from the said saphre" (*72*).

In his "Art of Glass," an English translation of which was published in 1699, Haudicquer de Blancourt, who was especially fond of blue because "it has resemblance to that of the Heavenly Arch and is taken for the Symbol of Generosity," gave specific directions for the preparation of metallic pigments used to tinge glass and "set it off with an unspeakable Beauty" (*73*). He told how Father Antonio Neri used to prepare "Zaffer" by heating the ore to redness in the furnace, sprinkling it with vinegar, grinding it, and washing it by decantation with warm water (*73*), (*74*). In his "Ars Vitraria Experimentalis" Johann Kunckel explained that the acetic acid used in this process was unnecessary and that the roasting of the ore served to remove the arsenic, which was then collected, resublimed, and sold in the apothecary shops (*70*).

Georg Brandt, the discoverer of cobalt, was born in the spring of 1694 at Riddarhytta, Vestmanland, where his father, Jurgen Brandt, a former apothecary, operated a copper smelter, an iron-works, and some mines. At an early age Georg began to help his father with his chemical and metallurgical experiments. He studied medicine and chemistry for three years at Leyden under the famous Hermann Boerhaave and received his degree of doctor of medicine at Reims in 1726. Although he never carried on a general practice, he was one of the physicians called to the death-bed of Fredrik I (*5*), (*6*), (*34*).

On his way home from the Netherlands he studied mining and metallurgy in the Harz, and in 1727 he was placed in charge of the chemical laboratory at the Bureau of Mines in Stockholm, which was then in poor financial condition. After the laboratory was sold, Brandt and his students, Henrik Teofil Scheffer and Axel Fredrik Cronstedt, carried on their epoch-making researches at the Royal Mint, and in 1730 Brandt became assay-master of the Mint. Three years later he published a systematic investigation of arsenic and its compounds in which he showed that arsenic is a "semi-metal" and that "white arsenic" [arsenious oxide] is its calx (*35*).

Brandt's most important contribution to science was his discovery of the element cobalt. Since the mineral which had been used since the sixteenth century for making "Zaffer," or smalt, resembled copper ores in its ability to give blue solutions when dissolved in acids, yet (even in minute amounts) imparted a much deeper blue color to glass than copper compounds do, it was called "cobalt" from the German word *Kobold*, meaning *subterranean gnome*. These little, teasing earth sprites are frequently mentioned in Goethe's "Faust":

Salamander soll glühen	Salamander shall kindle,
Undene sich winden,	Writhe nymph of the wave,
Sylphe verschwinden,	In air sylph shall dwindle,
Kobold sich mühen.	And Kobold shall slave.
Wer sie nicht kennte	Who doth ignore
Die Elemente,	The primal Four,
Ihre Kraft,	Nor knows aright
Und Eigenschaft,	Their use and might,
Wäre kein Meister	O'er spirits will he
Über die Geister. (*8*)	Ne'er master be. (*8*)

The Kobolds, according to an ancient German superstition, delighted in destroying the work of the miners, causing them endless trouble; and in mining towns the people used to pray in the churches for deliverance from the power of these malicious spirits (7).

In 1730 or before, Georg Brandt prepared a dark blue pigment from an ore found at the Skilå copper works (Riddarhytta) in Westmanland (*39*). Specimens of this "färgcobalt" are still preserved in the Cederbaum collection at Oskarshamn. Since the first accurate description of metallic cobalt is to be found in Brandt's dissertation on the half-metals in the *Acta Literaria et Scientiarum Sveciae* for 1735, it has frequently been stated that cobalt was discovered in that year. Nils Zenzén has shown, however, that this issue of the *Acta* was not published until 1739 and that the portion of Brandt's "Diarium Chymicum" which records his researches from the latter part of 1737 to the end of 1738 is merely a Swedish edition of the *Dissertatio de semi-metallis*.

According to Zenzén, Brandt stated in his diary for 1741 (which was not edited until 1744): "As there are six kinds of metals, so I have also shown with reliable experiments, in my dissertation on the half-metals which I presented to the Royal Academy of Sciences in Upsala in 1735, that there are also six kinds of half-metals. The same dissertation shows that I, through my experiments, had the good fortune . . . to be the first discoverer of a new half-metal, namely cobalt regulus, which had formerly been confused with bismuth . . ." (*39*). Zenzén believes, however, that this date must be attributed to Brandt's lack of memory. After separating this metal by fire assay, he named it *cobalt* for the mineral from which he had extracted it. In his "Dissertation on the semi-metals" Brandt stated that six metals and six "half-metals" (mercury, bismuth, zinc, and the reguluses of antimony, cobalt, and arsenic) were then known. By a "half-metal" he meant a substance which resembles the metals in color, weight, and form but which is not malleable. Since most bismuth ores contain cobalt, he gave six ways of distinguishing between these two "semi-metals."

"1. When bismuth is broken with a hammer, it gives a fracture composed of little super-imposed laminae. The regulus of cobalt is more like a true metal. Moreover there is a very great difference in the color of these two metals. . .

2. In fusing they do not mingle at all with each other; it is easy to separate them with a stroke of the hammer; for they are attached about as an almond is to its stone; and in this union they seem to be separated by a segment of a circle so that they both appear to form but a single regulus, at one end of which is found the bismuth, or marcasite, and at the other the regulus of cobalt.

3. The regulus of cobalt, pulverized and calcined, gives, when one fuses it with flint and fixed alkali, a blue glass, known under the names *zaffera*, *sasre*, or *smalt*. Marcasite does not give any smalt. The blue glass which bismuth ore sometimes gives is produced by the cobalt which is almost always found in the ores of this semi-metal.

4. Bismuth melts easily; when kept fused, it becomes calcined like lead and converted into a yellow powder, which, when melted, gives a glass of the same color as that of lead. . .

5. Bismuth amalgamates with mercury; which the regulus of cobalt does not do at all.

6. Bismuth dissolves in nitric acid and in aqua regia; both solutions are precipitated by pure water in the form of a white powder. When the regulus of cobalt is dissolved in these menstrua, it cannot be precipitated from them except by the alkalies; fixed alkali precipitates it in the form of a powder which, after being washed, remains dark and black; whereas when one precipitates it with volatile alkali, especially if it has been dissolved by

aqua regia, it acquires a very red color, which changes to blue, if one exposes it to the fire up to the point of redness" (*27*).

Brandt later made a more complete investigation of cobalt. He also demonstrated that common salt and soda contain the same (mineral) alkali, whereas saltpeter contains the vegetable alkali. This confirmed the earlier work of Duhamel du Monceau. Brandt encouraged the use of Swedish zinc in the manufacture of brass. When he died at Stockholm on April 29, 1768, his death was mourned by the entire scientific world. He was one of the ablest chemists of his time (*6*).

A. F. Cronstedt once spoke eloquently of "what a Brandt in our time can accomplish in cramped quarters, with broad knowledge and with zeal which even age cannot check. This honored man, whose presence here prevents me from saying what I wish, received chemistry and its instruments (already rusting after Hjärne's death) with newer views in natural science, with thorough mathematical knowledge, and with systematic order such as his master Boerhaave of Leyden had employed. Thereafter, followed only experiments which all scholars could apply to experimental physics and from which husbandry could quickly benefit. The science was presented as clearly as it had formerly been made obscure, and from that day, it has gradually gained the right to instruct the youth in our universities, to the great gain of both parties" (*75*).

After Anton von Swab and Georg Brandt had died in the same year, Carl von Linné said: "The kingdom and our sciences have now lost in a single year two stars of the first magnitude, Brandt and Swab. The Bureau of Mines and the science of mining have lost their supporting pillars. Men such as these never spring up like mushrooms. So far as I know, Europe has none like them .... A king can lose an army, but within a year have another just as good. A king can lose a fleet and within two years have another rigged up, but a Brandt and a Swab cannot be gotten again during his entire reign" (*52*). The History of the Swedish Academy of Sciences describes Brandt as "frugal, taciturn, and solitary" (*76*).

In 1776 a Hungarian chemist, Petrus Madács, defended a thesis in which he claimed, as did J. J. Winterl, that cobalt is a compound of iron and arsenic, but admitted that nickel is an element. He distinguished clearly between copper and nickel and stated that "copper and arsenic never give nickel" (*77*).

Although chemists long disputed the elemental nature of cobalt, perhaps because they were unable to reduce the blue smalt to the metal, Torbern Bergman explained in 1780 that, because of the high coloring power of cobalt, only a small amount of it need be present in smalt. He heated many kinds of cobalt glass with black flux and was able, in each case, to obtain the metal, but only in small amounts (*78*). He distinguished definitely between nickel and cobalt, stated that nickel never gives a blue glass nor a sympathetic ink nor a red solution in acids and that cobalt never gives a green one, and that pure nickel readily alloys with silver, whereas cobalt does not (*78*). From experiments with the preparation of smalt and sympathetic ink in the following year, Sven Rinman also concluded that cobalt and nickel are two entirely different metals (*79*).

Nickel

Axel Fredrik Cronstedt, the discoverer of nickel, was born on December 23, 1722, in the province of Södermanland in Sweden (*5*). His father, a lieutenant-general, gave him a good education, and he soon demonstrated his ability in physical science and mathematics. He rendered great service to his country as a metallurgist in the Bureau of Mines, and his name will always be honored because of the brilliant manner in which he discovered the useful metal nickel (*6*), (*24*).

URBAN HIÄRNE, 1641-1724

Swedish physician, mineralogist, and poet. Assessor and later acting president of the Swedish Bureau of Mines. Author of "Regium Laboratorium Chymicum," Stockholm, 1683. In 1694 he mentioned the ore *Kupfernickel*, in which Cronstedt more than half a century later discovered nickel.

The history of this metal is similar to that of cobalt. An alloy of nickel called packfong (or paktong) was used by the Chinese long before the metal was known in Europe (*7*), (*23*). In Germany a heavy, reddish brown ore, frequently found covered with green spots or stains, was used to color glass green; the miners called it *Kupfernickel* (*21*). Since *Nickel*, like *Kobold*, means *deceptive little spirit*, the word *Kupfernickel* may be translated, *false copper*. Urban Hiärne, in a work on metals published in 1694, expressed a belief that Kupfernickel was a kind of cobalt or arsenic mixed with copper, but in this view there was only a germ of truth (*7*), (*24*). A. F. Cronstedt once said, "Hiärne in his lifetime pursued chemical research most zealously. With all his creative genius and his desire to support Cartesian natural science with chemical arguments and conclusions, he still did not fail to consider the practical use which industry could demand of it. With the support of the authorities, he therefore occupied himself with the testing and investigation of substances from all realms of nature and all parts of the country" (*75*).

Although no one had ever succeeded in extracting copper from *Kupfernickel,* J. H. Linck (or Link) stated in 1726 that, since it gives green solutions when dissolved in nitric acid, it must be a cobalt ore containing copper (*24*), (*80*) When Swedish cobalt miners found a reddish yellow ore which imparted little or no blue color when fused with glass frit, they called it "cobalt which had lost its soul" (*21*).

In 1751 Axel Fredrik Cronstedt investigated a new mineral which he found in the cobalt mine at Los, Färila parish, Hälsingland (*21*). In one of his experiments he placed a piece of iron in the acid solution of the ore, expecting to see the copper deposit on it. To his great surprise, he was unable to secure a deposit of any kind, for, as is now well known, niccolite contains no copper (*9*). Upon calcining the green crystals which covered the surface of some weathered Kupfernickel, and reducing the calx, or oxide, by heating it with charcoal, Cronstedt obtained a white metal bearing no resemblance whatever to copper. After studying its physical, chemical, and magnetic properties, he announced in the Memoirs of the Stockholm Academy that he had discovered a new metal, different from all others, for which he proposed the name nickel (*7*), (*21*).

BALTHASAR-GEORGES SAGE
1740–1824

French analytical and mineralogical chemist of the phlogistic school. In his "*Analyse Chimique,*" published in 1786, he gave methods of testing and analyzing coal, clay, water, and many minerals.

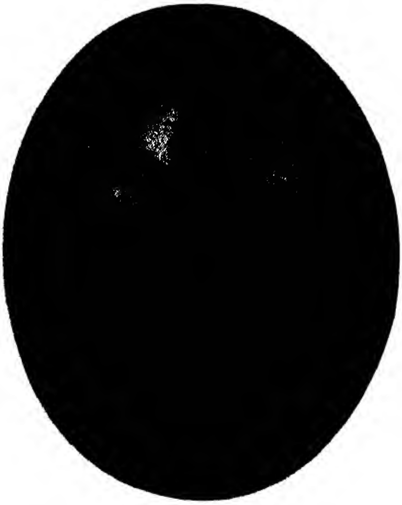
He said,

> This salt or this vitriol, after having been calcined, gives a colcothar or clear, gray residue which, when fused with three parts of black flux, gives a regulus of 50 pounds per quintal. This regulus is yellowish on the outside, but in the fracture it is silver-colored with iridescent colors, and composed of little laminae, quite similar to those of bismuth. It is

> hard and brittle, only feebly attracted by the magnet, calcination changes it to a black powder; these two properties come from the iron which has passed into the vitriol. This regulus dissolves in aqua fortis, aqua regia, and spirit of salt; it gives on dissolving a brilliant green color, and there precipitates a black powder which, when heated before the enamelers' blowpipe, gives signs of phlogiston and of the metallic part which it contains. . . . (*7*), (*21*).

The slight magnetization observed by Cronstedt is a property of nickel itself. In 1751 he mixed some Kupfernickel with "black flux," placed the mixture in a crucible, and covered it with a layer of common salt. Upon roasting it he not only reduced the oxide to the metallic state, but melted the metal. Not until 1754 did he publicly christen it. "The greatest quantity of the new previously described half metal," said he, "is contained in Kupfernickel; therefore I retain the same name for its regulus or call it *nickel* for short. For my experiments I have used a massive *Kupfernickel* from the Kuhschacht [Cow Shaft] in Freiberg, Saxony" (*21*). Kupfernickel, or niccolite, is now known to be an arsenide of nickel.

Many chemists in Sweden and in other parts of the world immediately accepted Cronstedt's claim to the discovery of a new element, but Sage (*22*) and Monnet in France believed that his nickel was merely a mixture of cobalt, arsenic, iron, and copper (*7*). As a matter of fact, it was somewhat contaminated with iron, cobalt, and arsenic; and therefore the great pioneer in analytical chemistry, Torbern Bergman, carried out an elaborate series of experiments by means of which he obtained nickel in a high state of purity. The results he published in 1775 completely confirmed those of Cronstedt, for he showed that no combination of iron, arsenic, cobalt, and copper will duplicate the properties of nickel. Bergman's pupil, Johan Arvidsson Afzelius, defended these views at Upsala in 1775 (*7*), (*36*).



TORBERN BERGMAN, 1735–1784

Swedish chemist, mineralogist, and editor. Author of the "*Opuscula physica et chemica*," a six-volume treatise. Among his students were Gahn, the discoverer of manganese; Hjelm, who isolated molybdenum; and the d'Elhuyar brothers, who discovered tungsten.

Even after this proof, some chemists were very conservative about accepting the new element. William Nicholson, in his "First Principles of Chemistry" published in 1796, gave the following account of it:

> This metallic substance has not been applied to any use; and the chief attention of those chemists

> who have examined it has been directed to obtain it in a state of purity; which, however, has not yet been accomplished. . . . Nickel has been thought to be a modification of iron. . . . So long as no one is able to produce this metal from pure iron or copper, and to explain in an intelligible way the process by which it can be generated, we must continue to regard it as a peculiar substance, possessing distinct properties. The general opinions of chemists concur in admitting the force of this reasoning (*10*).

Cronstedt's fame does not rest alone on his discovery of nickel, for he made an excellent classification of minerals which was translated into several languages. Berzelius said of him, "Cronstedt, the founder of the chemical system of mineralogy, a man who by his acuteness in that science rose so far above his age that he was never correctly understood by it, used the blowpipe to distinguish between minerals" (*11*). Ability to use this instrument skilfully and without fatigue and injury to health required, as Berzelius pointed out, an intensive training that few chemists care to undergo. Nevertheless, Cronstedt acquired such unusual control over it that he could direct a candle-flame upon a sample no larger than the head of a pin and make it white-hot (*11*). Jagnaux states that Cronstedt and Rinman operated a successful plant for distilling zinc, and that they "were as well versed in metallurgy as in mineralogy" (*4*). Cronstedt also discovered a zeolite, one of the silicates so widely used for softening water, and wrote a paper on it in 1756. He died in Säters parish near Stockholm on August 19, 1765 (*32*).

Manganese

When Cronstedt died, the man who is conceded to be the discoverer of manganese was exactly twenty years old. Johan Gottlieb Gahn was born at Voxna, an iron-mining town in South Helsingland on August 19, 1745 (*5*). Left fatherless at an early age and obliged to earn his living in the mines, he shared the joys and sorrows of the laborers and learned mining "on the lowest and wettest level" (*17*). He studied mineralogy under Bergman, became expert in the use of the blowpipe, and, according to Berzelius, always carried it with him, even on the shortest trips. When Gahn demon-

JOHAN GOTTLIEB GAHN
1745–1818

Swedish chemist, mineralogist, and mining engineer. Manufacturer of copper, sulfur, sulfuric acid, and red ochre. Discoverer of metallic manganese.

strated the presence of copper in certain kinds of paper by burning a quarter of a sheet, heating the ash with the blowpipe, and displaying a tiny speck of the red metal, the young Berzelius watched him with wonder and admiration (*11*). J. Nicklès believed, however, that this copper must have been volatilized from Gahn's burner (*40*).

Pyrolusite has been used for centuries in the manufacture of glass. After mentioning the production of blue glass with "zaffer" (a mixture of roasted cobalt ore and sand), Vannoccio Biringuccio wrote in his "Pirotechnia" in 1540, "There is still another half mineral of the same kind, so-called Braunstein. This comes from Germany and is found especially in Tuscany in Mt. Viterbo and at Salodiana in the neighborhood of Montecastello, near Cara. It is dark rust brown. It does not melt so that one can obtain metal from it. But when one adds vitrifiable substances to it, it colors them a handsome violet. The master glass-makers color their glasses a wonderful violet with it. The master potters also use it for violet decorations. Braunstein, moreover, when mixed with molten glass, has the special property of purifying it and making it white instead of green or yellow" (*57*). Because of the last-named property, glass-makers used to call it *sapo vitri*, or glass soap.

The Berlin glass and porcelain technologist, J. H. Pott, believed that pyrolusite consisted of phlogiston and an earth somewhat like that in alum (*58*). In 1740 he prepared "chameleon mineral" (potassium permanganate) and other compounds from it and showed that iron is not a constituent of pure pyrolusite (*13*).

The first person to prepare a little metallic manganese was probably Ignatius Gottfried Kaim, who described it in his dissertation, "De metallis dubiis," which was published at Vienna in 1770 (*12*). Although this publication is rare and inaccessible, P.-J. Macquer left an abstract of it in his famous chemical dictionary. By heating a mixture of one part of pulverized pyrolusite with two parts of black flux, Kaim obtained a bluish-white, brittle metal with countless shining facets of different shapes, showing in the fracture a play of colors from blue to yellow. He claimed that this regulus was free from iron (*59*). This incomplete research attracted little notice. The mineral was also known by the confusing names "black magnesia" and "manganese." Bergman knew, however, that it was not a compound of the alkaline earth, magnesia, for he said, "The mineral called black magnesia is nothing other than the calx of a new metal, which must not be confounded with lime nor with magnesia alba." He failed, however, in all attempts to reduce the ore (*13*), (*25*), and finally turned the problem over to his friend, Scheele, who in 1774, after experimenting for three years, presented his results to the Stockholm Academy in the form of a paper entitled, "Concerning Manganese and Its Properties." In this epoch-making dissertation he announced the existence of the gaseous element chlorine and paved the way for the discovery of oxygen gas and the metals, barium and manganese. Scheele stated that the mineral known as "manganese" was the calx of a metal different from any then known (*26*).

Although Pott, Bergman, and Scheele all believed in the existence of the metal manganese none of them were able to isolate it. However, in 1774 Gahn (*25*) lined a crucible with moist charcoal dust, placed in the center a mixture of the pulverized pyrolusite and oil, and covered it with more of the charcoal dust. After luting another crucible to this, he heated them intensely for an hour and, upon opening the apparatus, he found in it a button of metallic manganese weighing about a third as much as the ore from which he had isolated it (*13*), (*30*). For the accomplishment of this difficult reduction and for the isolation of this important metal, Gahn deserves high praise.

This discovery, like most of his others, was not published in any scientific journal. In his first attempts, Gahn obtained what Scheele called "reduced pyrolusite . . . combined with much phlogiston and a little iron." On May 16, 1774, Scheele sent him some purified pyrolusite with the suggestion, "I am eagerly waiting to see what kind of result this pure Braunstein will give when you apply your hell-fire to it, and I hope you will send me a little of the regulus as soon as possible" (*37*). On June 27th of the same year, Scheele thanked Gahn for the manganese regulus ["regulum magnesiae"] and added, "I believe that the Braunstein regulus is a half metal different from other half metals and closely related to iron" (*37*).

In his notes to H. T. Scheffer's chemical lectures, which were published in 1775, Torbern Bergman stated that a fifteenth metal had recently been added to the fourteen which Scheffer had discussed. Because of its weight, ability to color glass, and its precipitation with ferrocyanides (blodlut), Bergman had suspected that pyrolusite must contain a peculiar metal as an essential constituent. "At the same time," said he, "Hr. J. G. Gahn, without knowing of my reasons, actually brought forth from it by reduction a half metal which in refractoriness approaches nearest to platinum, and which, moreover, does not resemble any of those previously known . . . . Since then, I, too, have obtained the regulus of pyrolusite by reduction, but could not purify it from iron" (*38*).

In 1785 P. J. Hjelm published in the *Nya Handlingar* of the Swedish Academy of Sciences a detailed description of this reduction. He obtained his specimens from a pyrolusite quarry in Undenas parish in Vermland. After placing a mixture of a known weight of the pulverized sample with a little oil or melted tallow and powdered coal dust or blood charcoal in a large covered crucible lined with a mixture of iron-free clay and coal dust, he applied sufficient heat from his forge to volatilize the oil without allowing it to burst into flame. In less than an hour, he obtained a regulus which weighed more than half as much as the original crude pyrolusite. Assessor

Qvist suggested to him that the metal could be produced more economically in a cast steel furnace or wind furnace (*60*).

J. C. Ilsemann of Clausthal also obtained manganese independently without previous knowledge of the methods used by Gahn and Bergman. Ilsemann reduced 110 pounds of pyrolusite from Ilsefeld by heating it with a mixture of fluorspar, lime, powdered charcoal, and ignited salt, and obtained four and one-half pounds of impure metallic manganese from which he was unable to separate the iron (*61*).

In 1784 Gahn was made assessor at the College of Mines; he also served as deputy to the 1819 Diet, and was known politically as a Liberal (*14*). He was not only a brilliant chemist and mineralogist and a conscientious public official, but also a highly successful business executive. He owned and managed mines and smelters, and introduced new industrial methods; and it was in his sulfuric acid plant that Berzelius discovered the element selenium. During the American Revolution, when large amounts of pure copper were needed for sheathing ships, Gahn's plant at Stora Kopparberg was able to fill large rush orders (*15*). It is a curious fact that Assessor Gahn bore such a striking resemblance in features, gestures, and intellectual interests to Dr. William Hyde Wollaston, the English scientist who later discovered palladium and rhodium, that he was often called "the Wollaston of Stockholm" (*16*). Berzelius once stated, in fact, that one "would take them for sons of the same father" (*16*). Thomas Thomson, who once visited Assessor Gahn at his home in Fahlun, said that "his manners were the most simple, unaffected and pleasing of all the men of science" he had ever met, and that "benevolence and goodness of heart . . . . . beamed in his countenance."

When Edward Daniel Clarke visited Fahlun, he said that "perhaps in no part of the world" will the traveler "meet with superintendents so well informed . . . at the head of whom is the celebrated Gahn, whose acquirements, and the kindness he has always shewn to strangers, have entitled him to respect and consideration in all the Academical Institutions of Europe . . . . Hospitality in a Swede is what we may always expect; but the attention paid to strangers by Mr. Gahn, especially if their visits had any view to science, was of a more exalted nature. He not only shewed a zeal, as if actuated by a religious duty, to satisfy scientific inquiries; but he did more—he directed them; and himself endeavoured to stimulate the ardour of those with whom he conversed . . . by exciting and then gratifying their curiosity" (*55*).

At the time of his sixty-eighth birthday, Gahn received a novel congratulatory note from Berzelius, which read: "From Herr Assessor's last letter I was happy to find new support for the doctrine of definite proportions. Herr Assessor was 68 on August 19; the following day (the 20th) I became

34; now 34 × 2 = 68, from whence it follows that Herr Assessor is equal to a multiple of me by two . . ." (*56*).

Gahn, unfortunately, left most of his scientific work unpublished, leaving only a few papers on the blowpipe, on a sensitive balance, and on economy in the operation of smelters. He died in Stockholm on December 8, 1818, at the age of seventy-three years. In a biographical sketch in the "Annals of Philosophy," one may read this high tribute:

> To sum up the whole, we may safely say that he was alike eminent as a practical chemist and mechanic, as a patriot in public, and a friend in private life, as presiding over the interests of the miner and of the farmer, and in fine as the guardian and overseer of the large family of his native poor.* It will not indeed be easy to find another whose talents have been at once more brilliant and more useful, who has been more admired and more loved by his country, than John Gottlieb Gahn (*15*).

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* Assessor Gahn helped to establish the first poorhouse at Fahlun.

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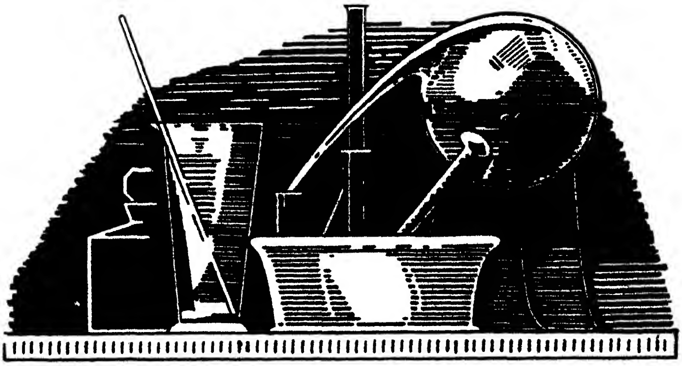

V. THREE IMPORTANT GASES

Chemists of the eighteenth century were intensely interested in "air," which they prepared by fermentation, by heating various chemical compounds, and by allowing substances of vegetable and animal origin to putrefy. Gradually the idea dawned that, as Priestley expressed it, there are "different kinds of air," and that Cavendish's "inflammable air from metals" is quite different from Daniel Rutherford's "noxious air" and from Scheele's "fire air." The preparation and recognition of the three gases, hydrogen, nitrogen, and oxygen, required true genius. For further information about Rutherford see pp. 106–20.

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> *"The generality of men are so accustomed to judge of things by their senses that, because the air is invisible, they ascribe but little to it, and think it but one remove from nothing."* (*1*)

In the latter part of the seventeenth century, Johann Joachim Becher and Georg Ernst Stahl advanced a peculiar theory of combustion that held sway over the minds of chemists for nearly a hundred years. They maintained that everything that can be burned contains a substance, phlogiston, which escapes in the form of flame during the combustion, and until Lavoisier overthrew this theory in 1777, practically all chemists believed that a metal consists of its calx, or oxide, and phlogiston. It was in this period of chemical history that the gases hydrogen, nitrogen, and oxygen were discovered.

From Bugge's "Das Buch der grossen Chemiker"

Georg Ernst Stahl
1660–1734

German chemist, physician, and professor. Co-founder of the phlogiston theory of combustion. Author of "*Fundamenta Chymiae Dogmaticae et Experimentalis.*" He distinguished between potash and soda and recognized that alum contains a peculiar earth different from all others.

Hydrogen

Hydrogen was observed and collected long before it was recognized as an individual gas. The statement of Paracelsus (1493–1541) that "*Luft erhebt sich und bricht herfür gleichwie ein Wind*"* has often been cited erroneously as an allusion to this gas (*2*), (*37*). Van Helmont, Boyle, Ma-

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* "Air rises and breaks forth like a wind."

yow, and Stephen Hales all had some slight acquaintance with hydrogen. In his "New experiments touching the relation betwixt flame and air," which were ready for publication in 1671, Robert Boyle dissolved iron in dilute hydrochloric or sulfuric acid and prepared hydrogen in the form of "inflammable solution of Mars [iron]" (*44*).

"Having provided a saline spirit [hydrochloric acid]," said Boyle, ". . . we put into a vial, capable of containing three or four ounces of water, a very convenient quantity of filings of steel, which were not such as are commonly sold in shops to chemists and apothecaries (those being usually not free enough from rust) but such as I had a while before caused to be purposely filed off from a piece of good steel. This metalline powder being moistened in the vial with a little of the menstruum, was afterwards drenched with more; whereupon the mixture grew very hot, and belched up copious and stinking fumes; which, whether they consisted altogether of the volatile sulphur of the Mars, or of metalline steams participating of a sulphureous nature, and joined with the saline exhalations of the menstruum, is not necessary to be here discussed. But whencesoever this stinking smoke proceeded, so inflammable it was, that on the approach of a lighted candle to it, it would readily enough take fire and burn with a blueish and somewhat greenish flame at the mouth of the vial for a good while together; and that, though with little light, yet with more strength than one would easily suspect" (*44*). Nicolas Lémery described it in 1700 in the Mémoires of the Paris Academy (*2*). In the 1686 English edition of his "Course of Chymistry," which was based on the fifth French edition, there is no mention of the evolution of any flammable or explosive gas when "vitriol of Mars" is prepared by dissolving iron in dilute sulfuric acid. At that time, Lémery merely observed that "the liquor heats and boils considerably" (*45*). In the eleventh French edition, however, which was published in 1716, a year after Lémery's death, the same preparation is described as yielding "white vapors which will rise to the top of the neck of the matrass; if one presents a lighted candle to

JOHANN JOACHIM BECHER
1635–1682

German chemist and physician. Founder of the phlogiston theory. His experiments on minerals are described in his "*Physica Subterranea.*" Stahl summarized his views on combustion in a book entitled "*Specimen Becherianum.*"

the mouth of this vessel, the vapor will immediately take fire and at the same time produce a violent, shrill fulmination" (*45*). In this reaction Lémery believed he had found the cause of thunder and lightning. In the posthumous 1701 edition of Turquet de Mayerne's complete works, the flammability of the gas is mentioned (*2*).

The name most closely associated with the early history of hydrogen is that of Mr. Henry Cavendish. Although he was a descendant of the Dukes of Devonshire and the Dukes of Kent, he was born at Nice; for his mother, Lady Anne Cavendish, had gone to France for the benefit of the mild climate. The date of his birth is given as October 10, 1731. The unfortunate death of Lady Cavendish two years later, and the consequent lack of maternal affection in the young child's life may account in some degree for the abnormal shyness and ungregariousness of the man. At the age of eleven years Henry Cavendish entered Dr. Newcome's school at Hackney, and from 1749 to 1753 he attended Cambridge University. Although he lacked only a few days of the necessary residence requirements, he left Cambridge without receiving a degree (*3*).

HENRY CAVENDISH
1731–1810

English chemist and physicist. This is the Alexander portrait. The likeness of Cavendish in W. Walker's engraving of British scientists was taken from the drawing by Tomlinson (*46*). Cavendish was the first to distinguish hydrogen from other gases and was an independent discoverer of nitrogen.

During his father's lifetime Cavendish lived on a meager allowance, but, upon his father's death in 1783, he received an enormous inheritance. Not long after this an aunt died, leaving him another large legacy. Thus he became, as Biot said, "the richest of all the learned and the most learned of all the rich" (*4*). Since Cavendish lived very modestly, the interest on his money accumulated until, at the time of his death, he was the largest depositor in the Bank of England (*5*).

It may be said without exaggeration that, of all great personages of scientific history, Mr. Henry Cavendish was the most singular. He was shy and awkward among strangers, and to him all men were strangers. The only social contacts he ever made were at the meetings of the Royal Society and at the Sunday evening receptions which Sir Joseph Banks was accustomed to give for the scientists in London. Cavendish spoke falteringly in shrill tones and was unable to converse with more than one person at a time; yet, because of his broad knowledge and clear reasoning, the members of the Royal Society all recognized him as a superior. Dr. Thomas Thomson in his well-known "History of Chemistry" cites a striking example of Cavendish's extreme fear of publicity. Dr. Ingenhousz once brought as his guest to the home of Sir Joseph Banks a distinguished Austrian scientist, whom he introduced to Cavendish with extravagant praise. The foreign guest, in turn, became profuse in his flattery of Cavendish, stating that he had come to London with the express purpose of meeting such a distinguished scientist, whereupon Cavendish, at first embarrassed, then utterly confused, darted through the crowd to his waiting carriage (5).

From Edward Smith's "Life of Sir Joseph Banks"

LADY BANKS SIR JOSEPH BANKS

(From a Wedgwood cameo, attributed to Flaxman.)

Sir Joseph Banks, 1743–1820. English naturalist and collector of plants and insects. President of the Royal Society from 1778–1820. His collections of books and natural history specimens were bequeathed to the British Museum. *Lady Banks* used to assist him in giving frequent receptions for the scientists of London.

A few scientists, however, knew how to overcome his extreme diffidence, and of these perhaps the most successful was Dr. Wollaston. "The way to talk to Cavendish," said he, "is never to look at him, but to talk as it were into vacancy, and then it is not unlikely but you may set him going" (6).

In spite of his love of solitude, Cavendish was not lacking in interest in the researches made by others. He presented young Humphry Davy with some platinum for his experiments, and went occasionally to the Royal Institution to see his brilliant experiments on the decomposition of the alkalies (*6*). Sir Humphry said later in his eulogy of Cavendish,

> .....Upon all subjects of science he was luminous and profound; and in discussion wonderfully acute......His name will be an object of more veneration in future ages than at the present moment. Though it was unknown in the busy scenes of life, or in the popular discussions of the day, it will remain illustrious in the annals of science, which are as imperishable as that nature to which they belong; and it will be an immortal honour to his house, to his age, and to his country (*7*).

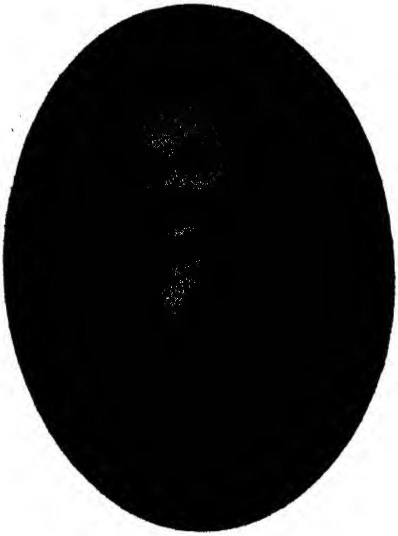
Cavendish dressed like an English gentleman of a bygone day. He wore a cocked hat and a gray-green coat with a high collar and frilled cuffs. His costume and personality are well depicted in the famous Alexander portrait, sketched hastily at a dinner without Cavendish's knowledge. Cavendish had three residences: one near the British Museum, furnished mainly with books and apparatus; another in Dean Street, Soho, containing his main library, which he generously placed at the disposal of all scholars who wished to use it; and a third dwelling known as Cavendish House, Clapham Common. This suburban home at Clapham, his favorite residence, he converted almost entirely into workshops and laboratories (*8*).

From Thorpe's "Scientific Papers of the Hon. Henry Cavendish"

CAVENDISH'S HOUSE AT CLAPHAM

Although many historians of chemical progress mention Cavendish as the discoverer of hydrogen, he himself made no such claim and prefaced his remarks on the explosibility of a mixture of hydrogen and air with the words, ". . . it has been observed by others. . ." He was, however, the first to collect gases over mercury (*41*) and distinguish hydrogen from other gases by the descriptive term, "inflammable air from the metals." His accurate description of its properties and his methods of obtaining the pure gas from different sources were scientific contributions of the first rank. He had, however, the mistaken idea that the hydrogen came from the metal rather than from the acid (*9*). He at first identified hydrogen with phlogiston, but later thought it was a compound of phlogiston and water.

Cavendish's death was as lonely as his life. He lived to the age of seventy-nine years, and then, one day, feeling the approach of death, he asked an attendant servant to leave the room and not return until a specified time. When the servitor returned, he found his great master dead (*10*). Mr. Henry Cavendish was given the honor of a public funeral and burial in All Hallows Church near the tomb of his philanthropic ancestor, Elizabeth Hardwicke. He lived a blameless life, unselfishly devoted to the advancement of science. His researches included electricity, astronomy, meteorology, and chemistry, and he was also well versed in mathematics, mining, metallurgy, and geology. He was a great scientist in the fullest sense of the word.



From Ramsay's "The Gases of the Atmosphere"

DANIEL RUTHERFORD, 1749–1819

Scottish physician, botanist, and chemist. Discoverer of nitrogen. Professor of botany at Edinburgh. President of the Royal College of Physicians of Edinburgh.

Nitrogen

The discovery of nitrogen was announced in a doctor's dissertation by Daniel Rutherford, uncle of Sir Walter Scott (*11*), (*40*). He was a son of Dr. John Rutherford, one of the founders of the Medical School at Edinburgh, and was born in that city on November 3, 1749. Preparatory to entering his father's profession, he graduated from the Arts course at the University of Edinburgh, and on September 12, 1772, he received the degree of doctor of medicine. His dissertation was the result of a research suggested and directed by the famous Scottish chemist, Dr. Joseph Black.

Dr. Black had noticed that when a carbonaceous substance was burned, a certain amount of air remained even after the "fixed air" (carbon dioxide) had all been absorbed by caustic potash. He therefore gave to Rutherford the problem of studying the properties of this residual "air" (*12*), (*38*).

Rutherford found that when a mouse was left in a confined volume of air until it died, one-sixteenth of the volume disappeared; and that when the remaining air was treated with alkali, it, in turn, lost one-eleventh of its volume. After thus removing the carbon dioxide ("fixed, or mephitic, air") and most of the oxygen, he studied the properties of the residual gas. He found it very difficult "to completely saturate air with phlogiston" (to remove all the oxygen), for after a mouse had died in it, a candle would burn feebly, and after the flame had flickered out, the candle wick or phosphorus would continue to glow. His best results were obtained by burning phosphorus in the confined air. Since the residual gas did not support life, he called it "noxious," or injurious, air. He did not realize, however, that his "noxious air," or nitrogen, as it is now called, is the constituent of the atmosphere that remains after removal of the oxygen and carbon dioxide. He thought that the "noxious air" was atmospheric air that had taken up phlogiston from the substance that had been burned. According to Rutherford, " . . . this conjecture is confirmed by the fact that air which has served for the calcination of metals is similar, and has clearly taken away from them their phlogiston." He thought that the "mephitic air" obtained by burning carbonaceous material contained less phlogiston than the "noxious air" remaining after combustion of phosphorus. Rutherford's epoch-making thesis, "*Dissertatio Inauguralis de Aere fixo dicto, aut mephitico*," is preserved in the British Museum (*12*),

Courtesy Lyman C. Newell

JOSEPH BLACK, 1728–1799

Scottish chemist, physicist, and physician. Professor of chemistry at Glasgow. He discovered carbon dioxide ("fixed air"), and distinguished between magnesia and lime. He discovered the latent heats of fusion and vaporization, measured the specific heats of many substances, and invented an ice calorimeter.

(*39*) and at the University of Edinburgh and has been translated into English.

After completing his medical course, Dr. Rutherford traveled for three years in England, France, and Italy. Upon returning to Edinburgh in 1775 he began his medical practice, and never again engaged in chemical research. Eleven years later he accepted the chair of botany at Edinburgh, but continued to practice medicine. He served for a time as president of the Royal College of Physicians of Edinburgh. Dr. Rutherford had a pleasant disposition, and displayed true loyalty and friendship toward his honored teacher, Dr. Black (*12*).

Although most authorities agree that Dr. Rutherford was the discoverer of nitrogen, it would be unfair to disregard the work of Scheele, Cavendish, and Priestley. Scheele obtained nitrogen at about the same time by absorbing the oxygen of the atmosphere in liver of sulfur or a mixture of sulfur and iron filings (*13*). One of Cavendish's papers, written before 1772 and marked in his handwriting "communicated to Dr. Priestley," describes his method of preparing "burnt air" by passing atmospheric air repeatedly over red-hot charcoal, and then removing the carbon dioxide by absorbing it in caustic potash. He studied the properties of nitrogen carefully, as shown by this accurate description: "The specific gravity of this air was found to differ very little from that of common air; of the two it seemed rather lighter. It extinguished flame, and rendered common air unfit for making bodies burn in the same manner as fixed air, but in a less degree, as a candle which burnt about 80″ in pure common air, and which went out immediately in common air mixed with $^{6}/_{56}$ of fixed air burnt about 26″ in common air mixed with the same portion of this burnt air" (*14*). It is probable that Rutherford was unacquainted with Priestley's earlier work on nitrogen (*38*), (*39*).

In his "Simple Bodies of Chemistry," David Low, as late as 1848, expressed a belief in the compound nature of nitrogen, based on the curious reasoning that, since ammonia is derived from the organic kingdom, it must contain carbon, and that therefore nitrogen must consist of carbon and oxygen (*49*).

Oxygen

"When Air's pure essence joins the vital flood,
And with phosphoric Acid dyes the blood,
Your Virgin Trains the transient Heat dispart,
And lead the soft combustion round the heart;
Life's holy lamp with fires successive feed,
From the crown'd forehead to the prostrate weed,
From Earth's proud realms to all that swim or sweep
The yielding ether or tumultuous deep.
You swell the bulb beneath the heaving lawn,
Brood the live seed, unfold the bursting spawn;

Nurse with soft lap, and warm with fragrant breath
The embryon panting in the arms of Death;
Youth's vivid eye with living light adorn,
And fire the rising blush of Beauty's golden morn" (*50*).

Many books have been written about the discovery of oxygen. The Orientalist, Heinrich Julius Klaproth, a son of the famous German chemist, Martin Heinrich Klaproth, found a reference to this gas in a Chinese book written by Mao-Khóa about the middle of the eighth century after Christ. Mao-Khóa believed that the atmosphere is composed of two substances: Yânn, or complete air (nitrogen), and Ȳne, or incomplete air (oxygen). Ordinary air can be made more perfect by using metals, sulfur, or carbon to rob it of part of its Ȳne. He said that when these substances burn in air, they combine with the Ȳne, which, according to Mao-Khóa, never occurs free, but is present in certain minerals and in saltpeter, from which it can be driven out by heating (*15*), (*34*). Signor Muccioli (*36*), however, has questioned the authenticity of this Chinese manuscript.


From Jean Paul Richter's "Leonardo"

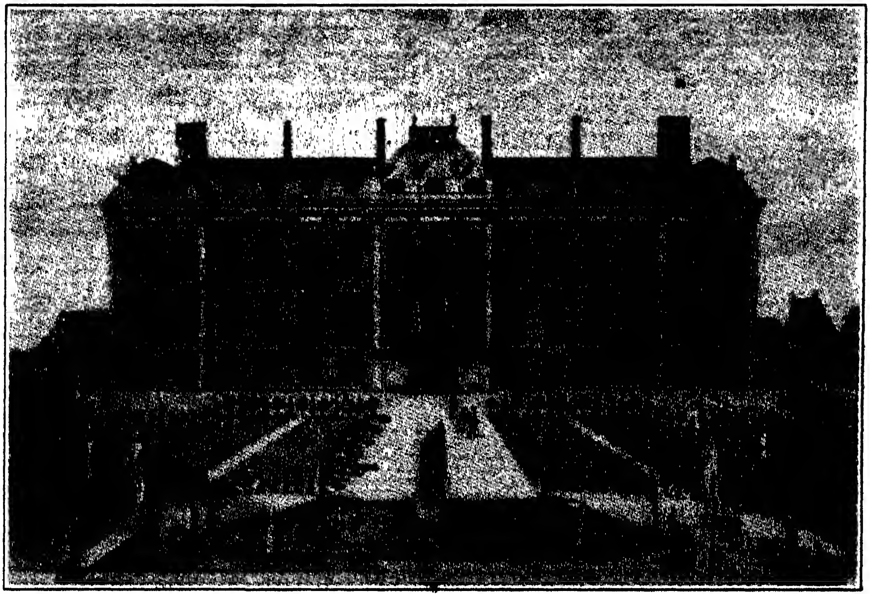
LEONARDO DA VINCI
1452–1519

(From a drawing in red chalk by himself. In the Royal Library, Turin.) Italian artist, sculptor, anatomist, and scientist of the first rank. Pioneer in mechanics and aëronautics. The first European to recognize that the atmosphere contains at least two constituents.

The first European to state that air is not an element was the versatile artist-scientist, Leonardo da Vinci (1452–1519). Leonardo, keen observer that he was, noticed that air is consumed in respiration and combustion, but that it is not *completely* consumed (*15*), (*35*).

Robert Hooke (*16*), in his famous book "Micrographia" published in 1665, gave a complete theory of combustion. He thought that air contains a substance (oxygen) that exists in solid form in saltpeter, and a larger quantity of an inert substance (nitrogen). Dr. John Mayow, when only thirty-three years of age, explained combustion by saying that air contains a *Spiritus nitro-aereus* (oxygen), a gas that is consumed in respiration and burning, with the result that substances no longer burn in the air that is left. He thought that his *Spiritus* was present in saltpeter, and stated that it existed, not in the alkaline part of the salt, but in the acid part. According to Dr. Mayow, all acids contain the *Spiritus*, and all animals absorb it into their blood as they breathe (*17*). T. S. Patterson, however, who has made an exhaustive study of Dr. Mayow's writings, believes that his contributions to the theory of combustion have been greatly over-estimated (*18*).

The first person to prepare oxygen by heating saltpeter was Ole Borch, but he did not know how to collect it (*19*). He stated in 1678 that it did not burn but that it made charcoal burn very vigorously (*51*). In his "Prominent Danish Scientists," V. Meisen shows a facsimile of the introduction to Borch's "Nitrum non inflammari," which was published in volume five of Thomas Bartholin's *Acta Medica;* "In a little book *Naturalis Historia Nitri* (Authore Guilielmo Clarcke Anglo, Francofurti et Hamburg 1675.8°. p. 13), a man of learning says: 'Saltpetre is ignitible, because experience shows that if a small piece of it is cast into a fire, it is ignited at once and burns, leaving a rest of lime or ash. It catches fire suddenly and blazes lively; and it burns downwards, whereas ordinarily fire always burns upwards.' In numberless experiments I have however found nothing of the kind . . ." (*52*).



From Gunther's "Early Science in Oxford," Vol. 7

ROBERT HOOKE'S HOME, MONTAGUE HOUSE, WHICH AFTERWARD BECAME THE FIRST HOME OF THE BRITISH MUSEUM

William Clarke's "Treatise on the Natural History of Nitre" was first published in London in 1670. A Latin translation of it was issued in 1675. Borch was a great physician, botanist, chemist, philologist, and historian of science who bequeathed all his property to the University of Copenhagen for the erection and maintenance of Borch's Collegium, a dormitory for students deserving of financial aid (*52*). Stephen Hales also prepared oxygen from saltpeter and collected it over water, but thought he had ordinary air; he did not believe in the existence of a "vivifying spirit" in the atmosphere (*19*). In April, 1774, there appeared in Abbé Rozier's *Journal de Physique* a remarkable paper by Pierre Bayen, a pharmacist who later became a medical inspector in the armies of the French Republic. In discussing his experiments with mercuric oxide, Bayen stated that, when mercury is calcined, it does not lose phlogiston, but combines with a gas and increases in weight. He thus rejected the phlogiston theory three years before it was proved false by Lavoisier (*20*).

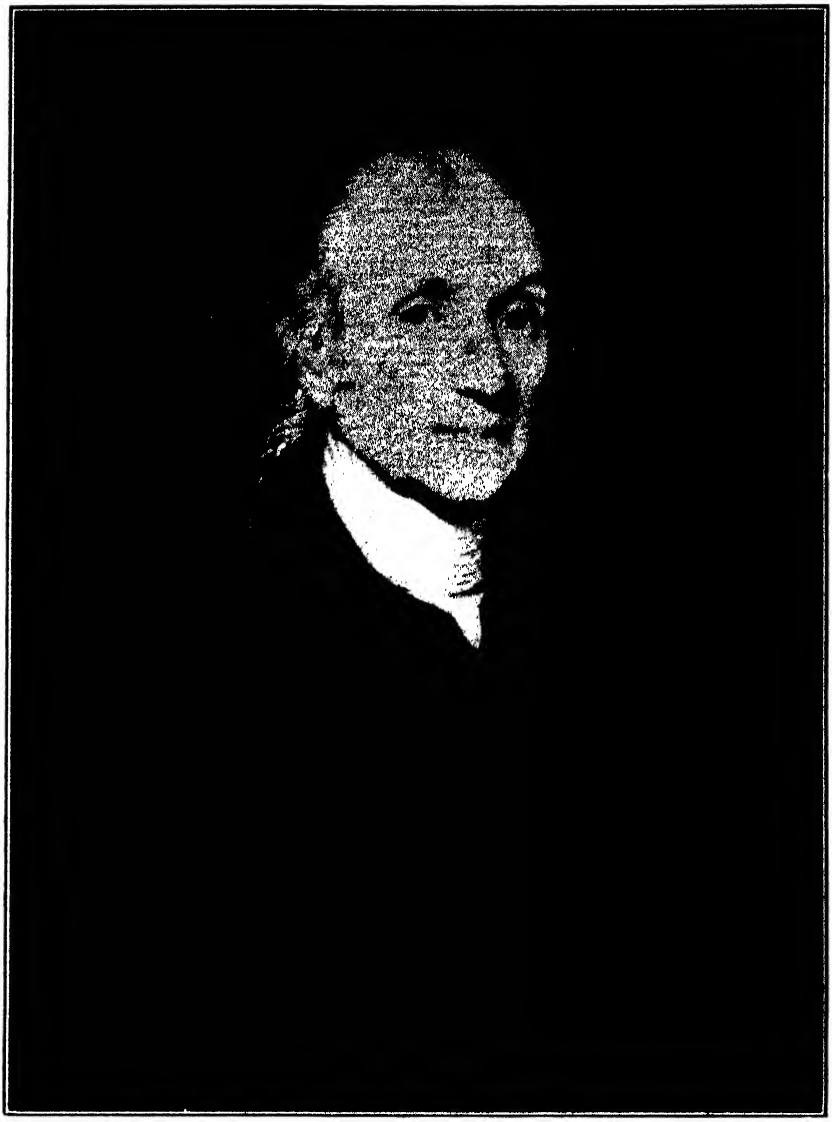
Courtesy E. R. Riegel

1641–1679

English chemist and physician, who died quite young. Famous for his early researches on combustion and respiration. His theory of combustion was described in his tract entitled "*De Sale Nitro et Spirito Nitro-aereo*" in 1674 (*48*).

Bayen, however, like all his predecessors who had handled oxygen, neglected to make a thorough study of its properties and failed to recognize it as a new substance. As Patterson says, he ". . . cannot therefore be regarded as having discovered it, and this applies with greater force to other unconscious preparations of oxygen by Hales and possibly by Robert Boyle, and, of course, still more strongly to the vague speculations of Hooke and Mayow" (*18*).

Most chemists agree that the actual discovery of oxygen was made independently at about the same time by Priestley in England and Scheele in Sweden. Priestley's results, to be sure, were published before those of Scheele, but Scheele's publisher had been inexcusably negligent. The question of

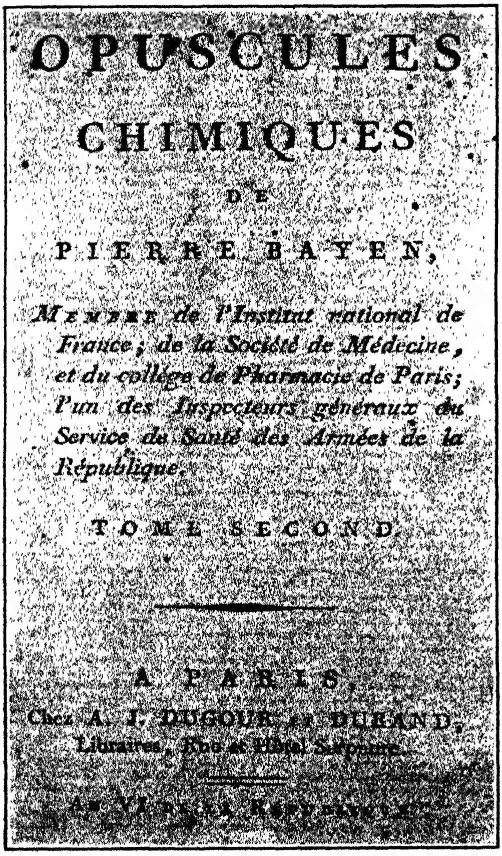


THE STUART PORTRAIT OF JOSEPH PRIESTLEY, 1733–1804

"Oh what an active brain had he,
And clear discriminating mind.
Through life his great desire was this:
To bless and elevate mankind" (54).

Joseph Priestley was born in Fieldhead, a tiny hamlet near Leeds, on March 13 (old style), 1733, and was therefore about one and one-half years older than that other great pioneer in pneumatic chemistry, Mr. Henry Cavendish. Although Priestley and Cavendish had similar scientific interests, their lives and personalities offered the greatest possible contrast. Since Priestley's mother died when he was only six years old, he was entrusted to the care of an aunt, Mrs. Keighley, of whom he afterward said that she "knew no other use of wealth, or of talents of any kind, than to do good" (*21*).

At the age of nineteen years he was sent to the Dissenting Academy at Daventry to be educated for the liberal ministry. After completing the three-year course, he ministered to congregations at Needham Market and later at Nantwich, but with small success. In 1761 he received an appointment as teacher of languages in the Dissenting Academy at Warrington, and taught Latin, Greek, French, Italian, oratory, and civil law. Although these subjects were only distantly related to the science in which he later won undying fame, Priestley's scientific spirit manifested itself even here—he encouraged absolute freedom of speech among his students.



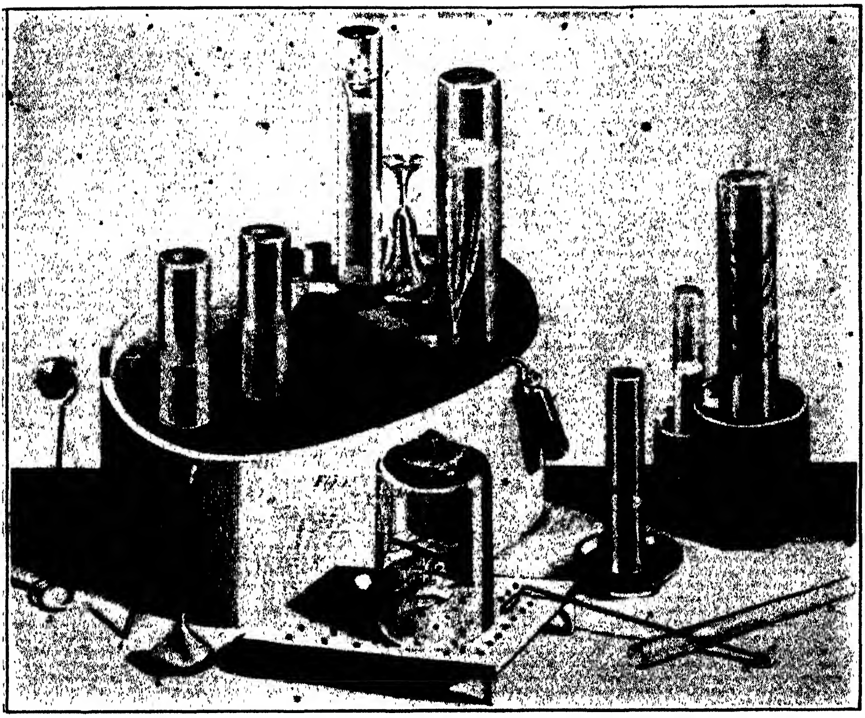
OPUSCULES
CHIMIQUES
DE
PIERRE BAYEN,
Membre de l'Institut national de France; de la Société de Médecine, et du collége de Pharmacie de Paris; l'un des Inspecteurs généraux du Service de Santé des Armées de la République.
TOME SECOND.

A PARIS,
Chez A. J. DUGOUR et DURAND, Libraires, Rue et Hôtel Serpente.

An VI de la République.

TITLE PAGE OF BAYEN'S "*Opuscules Chimiques*"

Even when struggling with poverty at Nantwich, Priestley loved to make experiments; and from his meager salary he purchased an air-pump and an electrical machine. In 1766 an event occurred that caused him to devote the rest of his life to scientific research. That event was his introduction to the great American statesman and scientist, Benjamin Franklin. Not long after this meeting, Priestley accepted a pastorate at Leeds. Since the parsonage happened to be located next door to the Jakes and Nell Brewery, the Reverend Mr.



From Priestley's "Experiments and Observations on Different Kinds of Air," 1774 and 1790
See references (9) and (22)

Priestley's Apparatus for Studying the Composition of the Atmosphere

Fig. 1, *a*, Earthenware pneumatic trough, 8" deep; *bb*, flat stones, which in his later wooden trough were replaced by a shelf for holding the jars; *cc*, jars, 10" × $2^{1}/_{2}$", for collecting gases; *d*, tall beer glass containing enough air to sustain a mouse for from 20 to 30 minutes, and "something on which it may conveniently sit, out of reach of the water." The mouse was introduced by passing it quickly through the water; *e*, gas generator heated by a candle or a red-hot poker.

Fig. 2, "Pots and tea-dishes" to slide under the gas-filled jars when removing them from the trough.

Fig. 3, Receiver for keeping the mice alive. It was open at top and bottom, except for plates of perforated tin, the lower of which stood on a wooden frame to permit circulation of air. To avoid chilling the mice, this receiver was kept on a shelf over the kitchen fireplace.

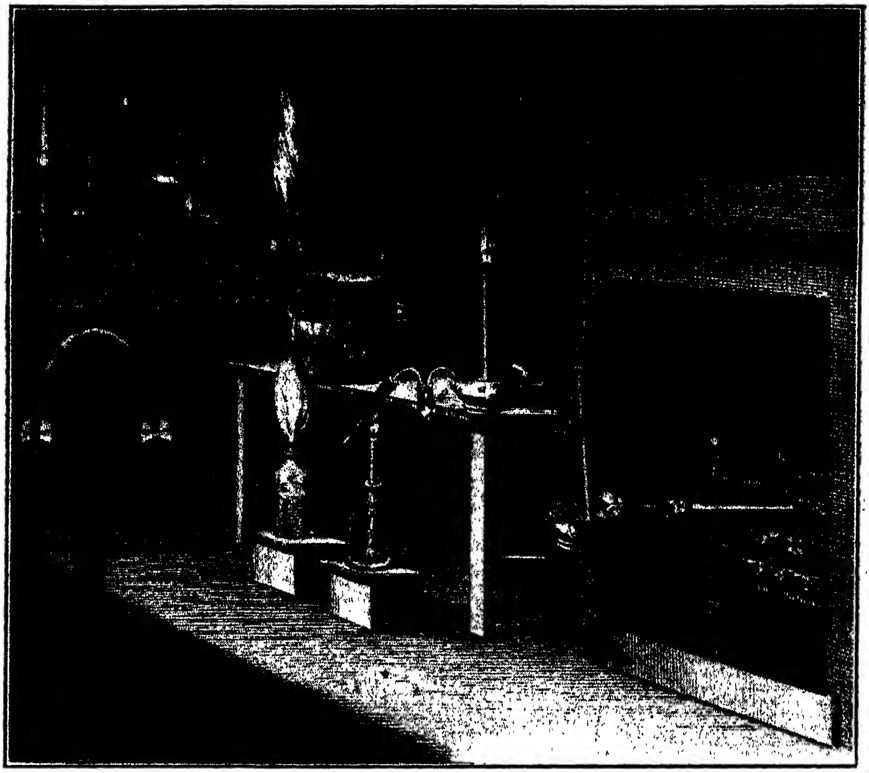
Fig. 4, Cork for closing a phial of solid or liquid which must be transferred, without wetting the contents, to a jar of gas in the pneumatic trough.

Fig. 5, Wire stand for supporting a gallipot inside a jar of gas.

Fig. 6, Funnel for "pouring air" into a glass jar by displacement of water.

Fig. 11, Glass cylinder for admitting a candle to test the ability of the gas to support combustion.

Fig. 12, *a*, Wax candle, bent for introducing it into a vessel, with the flame upward; *b*, wire; *c*, candle to be held under a jar standing in water. It was removed the instant the flame was extinguished, to avoid contamination of the gas in the jar with smoke.



Frontispiece of Priestley's "Observations on Different Kinds of Air," 1774 and 1790
See references (9) and (22)

PRIESTLEY'S LABORATORY

Fig. 7, Apparatus for expelling gas from solids. The fireplace was used for heating a gun barrel containing dry sand which had previously been ignited. The open end of the gun barrel was luted to the stem of a tobacco pipe leading to a trough of mercury.

Fig. 8, *a*, Trough containing an inverted cylinder, *b*, of mercury; *c*, a phial containing substances from which a gas may be liberated; *d*, glass trap to intercept moisture.

Fig. 9, Bladder for transferring gases. It contained a bent glass tube at one end and at the other a one-hole cork to admit a funnel. After the gas had been admitted, the bladder was tied tightly with string.

Fig. 10, *a*, Apparatus for impregnating a fluid with gas; *b*, bowl containing a quantity of the same fluid; *c*, phial containing chalk, cream of tartar, or pearlash, and dilute sulfuric acid for generating carbon dioxide; *d*, flexible leather tube, which permitted Priestley to shake the gas generator, *c*.

Fig. 13, Siphon.

Fig. 14, Evacuated bell jar.

Fig. 15, Apparatus for measuring small quantities of gas in his experiments with "nitrous air" (nitric oxide). *a*, small glass tube; *b*, wire; *c*, sharply bent, thin plate of iron for withdrawing the wire. This little apparatus was introduced under water into a jar of nitric oxide, and when the wire was withdrawn, nitric oxide took its place. Priestley measured the lengths of the columns of air, of nitric oxide, and of the resulting nitrogen peroxide after admixture.

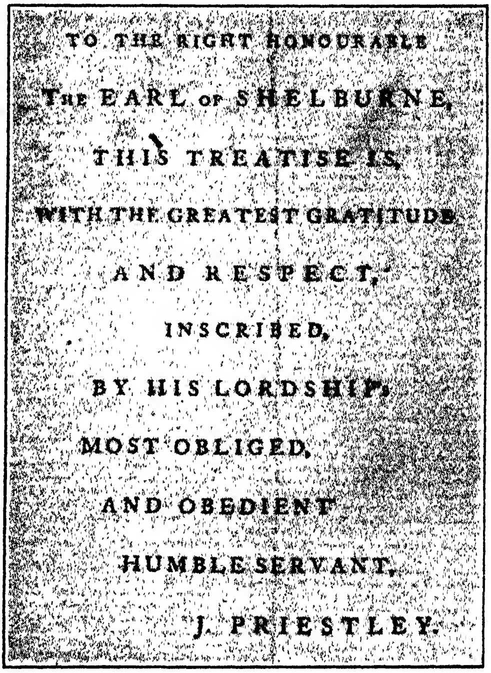
Fig. 16, Apparatus for taking the electric spark in any kind of gas. *a*, Mercury column; *b*, brass knob.

Figs. 17, 18, and 19 are different forms of apparatus for taking the electric spark in gases. Fig. 19 represents a mercury-filled siphon containing an iron wire, *aa*, in each leg. Any gas which was introduced would rise to *bb*, the upper part of the siphon. The mercury basins could be made part of an electric circuit.

Priestley had a convenient source of "fixed air" for his experiments. He soon discovered the pleasant taste of water charged with this gas, and recommended the refreshing beverage to his friends. Dr. William Brownrigg had previously made the same discovery (*22*), (*47*).

Inspired by Priestley's illuminating experiments with oxygen, carbon dioxide, and other gases, the great Spanish physicist, historian, and poet, Father José de Viera y Clavijo (1738–1799), praised him in a long poem. Although the following prose translation of an excerpt from it cannot render justice to the poetry, it nevertheless illustrates an early intellectual bond between the scientists of Spain, Italy, England, and the United States of America.

"If by His mandate Torricelli
Poised air's vast sea in slender tube,
Newton with his wondrous prism
Dawn's seven rays dissected out,
Jove's thunder and Heaven's ether
Yielded to Franklin's rod,
God also guided Priestley when He said:
Take thou this earth, take from it the fixed air" (*53*).*


TO THE RIGHT HONOURABLE
THE EARL OF SHELBURNE,
THIS TREATISE IS,
WITH THE GREATEST GRATITUDE
AND RESPECT,
INSCRIBED,
BY HIS LORDSHIP'S
MOST OBLIGED,
AND OBEDIENT
HUMBLE SERVANT,
J. PRIESTLEY.

DEDICATION OF PRIESTLEY'S "EXPERIMENTS AND OBSERVATIONS ON DIFFERENT KINDS OF AIR," 1774

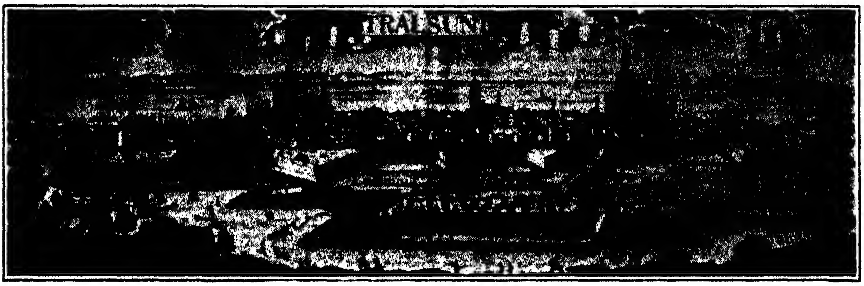
From 1772 to 1779 Priestley served as literary companion to Lord Shelburne. His most important chemical experiments, culminating in the discovery of oxygen, were made during this period, and his book entitled "Experiments and Observations on Different Kinds of Air" was therefore affectionately dedicated to Lord Shelburne. In 1780 Priestley became minister to a large metropolitan con-

---

* *"Si él hizo á Torricelli que pesase*
En tubo estrecho el mar de la atmosfera;
Que Newton con un prisma disecase
Los siete rayos de la luz primera;
Que Franklin con su barra le robase
El rayo á Jove, el Eter á la esfera;
También guió á Priestley, quando le dixo:
Toma esa tierra, saca el Ayre fixo . . ." (*53*).

gregation in Birmingham. Here he was contented in his ministry and happy in his association with such men as James Watt, Josiah Wedgwood, and Erasmus Darwin at the meetings of the Lunar Society, which met on the first Monday evening after each full moon in order that the members might find their way home through the unlighted streets. At Birmingham he completed his six-volume work on "Different Kinds of Air," which was later abridged to three volumes.

The struggles of the American and French revolutionists aroused Priestley's sympathy, and he was no dissembler. On July 14, 1791, about eighty persons had a dinner at a Birmingham hotel in observance of the second anniversary of the fall of the Bastille. A mob shattered the windows with stones. Although Priestley did not attend the dinner, his political views were well known. The fanatics broke up the meeting at the hotel, surged through the streets of Birmingham, burned Priestley's church, home, and library, and shattered his apparatus. Even then their thirst for violence was not satiated, and furious rioting continued for three days. Before the dragoons were at last able to disperse the mob and restore order, the homes and churches of many dissenters had become charred ruins (*23*).



From Zekert's "Carl Wilhelm Scheele, Sein Leben und seine Werke"

STRALSUND, THE BIRTHPLACE OF SCHEELE*

With the aid of friends, the Priestley family escaped without personal injury. After three unhappy years in London, they finally succeeded in collecting a small indemnity from the British Government, and emigrated to America (*23*). Priestley's last days were spent in the peaceful town of Northumberland, Pennsylvania, where he worked without interference at his beloved experiments (*33*). He died on February 6, 1804, and was buried in the Quaker cemetery at Northumberland.

Since Priestley found that some gases can be collected over water while others require mercury (*41*), he concluded that there must be different kinds of "airs." On August 1, 1774, he heated mercuric oxide with a burning glass, liberated a gas, "dephlogisticated air" (oxygen), and collected it

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over water. In an atmosphere of this gas, substances burned more brilliantly than in air. Five years later he tested the respirability of his "dephlogisticated air" by mixing it with nitric oxide over water. He found that much more nitric oxide was required to render a given volume of "dephlogisticated air" unfit for a mouse to breathe than for an equal volume of atmospheric air. His description of the experiment is charmingly naïve:

> My reader will not wonder that, after having ascertained the superior goodness of dephlogisticated air by mice living in it, and the other tests above mentioned, I should have the curiosity to taste it myself. I have gratified that curiosity by breathing it, drawing it through a glass syphon, and by this means I reduced a large jar full of it to the standard of common air. The feeling of it to my lungs was not sensibly different from that of common air, but I fancied that my breast felt peculiarly light and easy for some time afterwards. Who can tell but that, in time, this pure air may become a fashionable article in luxury? Hitherto only two mice and myself have had the privilege of breathing it (*24*).

From Zekert's "C. W. Scheele, Sein Leben und seine Werke"

YOUTHFUL PORTRAIT OF CARL WILHELM SCHEELE, 1742–1786*

Swedish pharmacist and chemist. Independent discoverer of oxygen. He discovered arsenic acid, distinguished between nitric and nitrous acids, demonstrated the presence of tartaric, citric, malic, and gallic acids in plants, and discovered lactic and uric acids in the animal realm.

On the one hundredth anniversary of the discovery of oxygen, a large audience assembled in Birmingham for the unveiling of a statue of Joseph Priestley, and an eloquent eulogy and biographical sketch was delivered by Thomas Huxley (*25*). At the same time the scientists of Leeds assembled at Priestley's birthplace and the chemists of America gathered at his grave near the banks of the Susquehanna to honor his memory (*26*). The meeting in Pennsylvania was memorable not only because it marked the centennial of the discovery of oxygen but also because it resulted in the founding of the American Chemical Society.

Carl Wilhelm Scheele was born on December 9, 1742, in Stralsund, then

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the capital of Swedish Pomerania. He was the seventh child in a family of eleven, and, since the family was not as rich in worldly goods as in children, he was apprenticed at the age of fourteen years to an apothecary named Bauch. Like other pharmacists of his time, Bauch prepared his own medicines from the crude drugs and was well versed in chemistry. In his laboratory were to be found many inorganic salts, the mineral acids, a few ores, rock-crystal, phosphorus, sulfur, benzoic acid, and camphor. His chemical library included the works of Boerhaave, Lémery, Kunckel, and Neumann (*27*). The fourteen-year-old apprentice soon developed a passion for reading chemical books and repeating the experiments described in them. His memory for chemical facts was so great that, after reading a book through once or twice, he had no need to consult it again.

In 1768 Scheele took charge of the Scharenberg pharmacy in Stockholm, and at about the same time he met with bitter disappointment at the hands of the Stockholm Academy, which rejected two of his earliest papers because of the unmethodical style in which they were written. The editor who refused them was Torbern Bergman, who afterward became Scheele's lifelong friend (*27*). In 1773 Scheele accepted a position in Lokk's pharmacy at Upsala. One day Lokk noticed that saltpeter which has been fused for some time remains neutral, but evolves red fumes when treated with vinegar. Assessor Gahn, the famous mineralogist who discovered manganese, was unable to explain the change, and Bergman, the illustrious professor of chemistry at Upsala, could give him no help. Scheele, however, readily explained that there are two "spirits of niter," or, as one says today, two acids, nitric and nitrous.

From Grimaux's "Lavoisier"
From the Painting by David

M. AND MME. LAVOISIER

In 1777 Lavoisier gave quantitative proof of the incorrectness of the phlogiston theory. Shortly after Priestley and Scheele discovered oxygen, Lavoisier gave the true explanation of combustion and respiration. Berthollet, Guyton-Morveau, Fourcroy, and Klaproth were among the first to accept the new views.

Gahn and Scheele became close friends, and much of their correspondence has been preserved. It was through Gahn that Scheele made the acquaintance of Bergman. When Scheele explained that potassium nitrate is converted by fusion into the deliquescent salt, potassium nitrite, Bergman became deeply interested in the young chemist, and they, too, formed a lasting friendship. Bergman received much of his practical instruction from Scheele, while Scheele's intellectual interests were broadened by his long association with the scholarly Bergman (*27*).

In spite of many offers from universities, Scheele never exchanged the practice of pharmacy for an academic career. The pharmacies of his day were quiet centers of original research, and as Scheele himself once said to Assessor Gahn, "... To explain new phenomena, that is my task; and how happy is the scientist when he finds what he so diligently sought, a pleasure that gladdens the heart" (*28*).

His most brilliant discoveries were made at the Lokk pharmacy. His notebooks, which have since been edited and published by Baron Nordenskiöld, show that he prepared oxygen in 1771 and 1772, that is to say, at least two years before Priestley did. Scheele made it by heating silver carbonate, mercuric carbonate, mercuric oxide, niter, and magnesium nitrate, and by distilling a mixture of manganese dioxide and arsenic acid. When oxygen is prepared by heating silver or mercuric carbonate, the carbon dioxide must be absorbed in caustic alkali.


A STATUE OF LAVOISIER WHICH FORMED PART OF THE FRENCH EXHIBIT AT THE SAN FRANCISCO EXPOSITION IN 1915

The results of these experiments were discussed in the book, "Fire and Air," which Scheele sent to his publisher, Swederus, near the end of 1775, but the book did not appear until 1777. In August, 1776, Scheele, exasperated at the delay, wrote dejectedly to Bergman, "I have thought for some time back, and I am now more than ever convinced, that the greater number of my laborious experiments on fire will be repeated, possibly in a somewhat different manner, by others, and that their work will be published sooner than my own, which is concerned also with air. It will then be said that my experiments are taken, it may be in a slightly altered form, from their writings. I have Swederus to thank for all this" (*29*). Scheele's discovery of oxygen was anticipated, as he had feared, but he is universally recognized as an independent discoverer of that gas.

In 1776 he became a provisor of the pharmacy at Köping, a little town on the north shore of Lake Mälar. The owner, Heinrich Pohl, had died, leaving the shop to his young widow. Instead of finding the prosperous business he had expected, Scheele met the discouraging task of freeing the estate from heavy debt (*27*), but he finally placed the business on a sound financial basis and purchased it from the widow Pohl. By 1782 his name was known to all European scientists, and his financial condition permitted him to build a new home and a well-equipped laboratory. One of his sisters and Mrs. Pohl kept house for him.

The last years of his life were filled with intense suffering from rheumatism. When he realized that death was near, he married the widow Pohl in order that the estate which he had struggled so hard to save might return to her. He died two days later on May 21, 1786, at the age of forty-three years. His entire life had been devoted to chemistry, and in one of his letters to Gahn one may read, "*Diese edel Wissenschaft ist mein Auge*"* (*30*).

Scheele was a phlogistonist to the end of his life, and thought that phlogiston was similar to the imponderable ether of the physicists and that hydrogen was a compound of phlogiston and "matter of heat." It has been shown that certain seventeenth-century chemists were ahead of most eighteenth-century scientists in their understanding of the composition of the atmosphere and the nature of combustion and respiration. Even the three men who had contributed most toward an understanding of the atmosphere—namely, Cavendish, Priestley, and Scheele—clung to the end of their days to the outgrown phlogiston theory.

The great French scientist, Lavoisier, would have liked very much to be considered an independent discoverer of oxygen, but he himself may have felt the weakness of his claim. He wrote in his "*Mémoire sur l'Existence de l'Air dans l'Acide Nitreux,*" read on April 20, 1776, "Perhaps, strictly speaking, there is nothing in it of which Mr. Priestley would not be able to claim the original idea; but as the same facts have conducted us to diametrically opposite results, I trust that, if I am reproached for having borrowed my proofs from the works of this celebrated philosopher, my right at least to the conclusions will not be contested" (*31*). In his remarkable paper "On the Nature of the Principle That Combines with Metals during Their Calcination and Increases Their Weight," which he had read during the Easter season of 1775, he had announced that this principle is simply "the purest and most salubrious part of the air; so that if the air which has been

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* "This noble science is my guide."

fixed in a metallic combination again becomes free, it reappears in a condition in which it is eminently respirable and better adapted than the air of the atmosphere to support inflammation and the combustion of substances" (*32*).

This was the death blow to the phlogiston theory. Although Lavoisier discovered no elements himself, he was the first to assert that oxygen is an element. Moreover, his correct explanation of combustion so revolutionized the entire science of chemistry that, under the new stimulus, many new elements were discovered soon after his tragic death on the guillotine. For this great service scientists will always honor the name of Antoine-Laurent Lavoisier.

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VI. DANIEL RUTHERFORD AND HIS SERVICES TO CHEMISTRY*

Although the statement that nitrogen was discovered in 1772 by Daniel Rutherford appears in most histories of chemistry, this Scottish scientist has remained almost unknown to chemists. Nevertheless, the life story and personal character of Dr. Rutherford emerge from the correspondence of his distinguished nephew, Sir Walter Scott, in almost pleasing manner. Both Dr. Rutherford and his father served as physicians to the Scott family, and the great novelist's allusions to them combine admiration, sincere affection, and pardonable family pride.

Dr. Rutherford served as professor of botany at the University of Edinburgh from 1786 to 1819, and was thus contemporary with Joseph Black, Charles Hope, and John Robison. He invented an ingenious maximum and minimum thermometer which is described in many modern textbooks of physics. The tragic circumstances surrounding his sudden death were described by Sir Walter in numerous letters to members of his family.

In his doctor's thesis Rutherford made a clear distinction between nitrogen and carbon dioxide which most of his contemporaries had failed to observe. Henry Cavendish, however, had made this distinction somewhat earlier, but had failed to publish his results. The names of Priestley and Scheele are also intimately connected with the discovery of nitrogen.

. . . . . .

The correspondence of Sir Walter Scott, his family genealogy, and the ten-volume biography by his son-in-law, J. G. Lockhart, contain frequent allusions to Scott's grandfather, Dr. John Rutherford, one of the founders of the medical school at the University of Edinburgh, and to his uncle, Dr. Daniel Rutherford, who is usually regarded as the discoverer of the element nitrogen. In the genealogy of the Scott family one may read:

> By his first wife, Jean Swinton, Professor John Rutherford had a son, John, who died young, and a daughter Anne, who married† Walter Scott, writer to the Signet, and became the mother of Sir Walter Scott Bart. He married, secondly, on the 9th August, 1743, Anne M'Kay, by whom he had five sons and three daughters. . .Daniel Rutherford, second son of Professor John Rutherford, was born on 3rd November, 1749. Prosecuting medical studies at the University of Edinburgh, he early discovered the existence of a gaseous fluid, now known as nitrogen gas. . .*(1)*

Sir Walter Scott gave some of the same facts in the following passage from his autobiography:

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* Presented before the Division of History of Chemistry at the Washington meeting of the American Chemical Society, March 28, 1933.

† A facsimile of the marriage contract is to be found in ref. (*4*).

> In [April, 1758] my father married Anne Rutherford, eldest daughter of Dr. John Rutherford, professor of medicine in the University of Edinburgh. He was one of those pupils of Boerhaave to whom the school of medicine in our northern metropolis owes its rise, and a man distinguished for professional talent, for lively wit, and for literary acquirements. Dr. Rutherford was twice married. His first wife, of whom my mother is the sole surviving child, was a daughter of Sir John Swinton of Swinton, a family which produced many distinguished warriors during the middle ages, and which, for antiquity and honourable alliances, may rank with any in Britain. My grandfather's second wife was Miss Mackay, by whom he had a second family, of whom are now [1808] alive, Dr. Daniel Rutherford, professor of botany in the University of Edinburgh, and Misses Janet and Christian Rutherford, amiable and accomplished women. . .(*2*)

As might be expected, the Rutherfords, both father and son, served as physicians to the Scott family. When Sir Walter was only eighteen months old, his right leg became paralyzed, and, after the best physicians had failed in their attempts to restore the use of it, his grandfather, Dr. John Rutherford, had him sent to live in the country (*3*), (*4*). During a serious illness in later life, Scott "submitted without a murmur to the severe discipline prescribed by his affectionate physician [Dr. Daniel Rutherford]. . ." (*5*).

John Rutherford was born in the Manse of Yarrow, Scotland, on August 1, 1695, was educated at the grammar school at Selkirk, and studied anatomy, surgery, and materia medica in London and later in Leyden under Boerhaave. After receiving his medical degree from the University of Reims in 1719, he went to Edinburgh to engage in private practice. In November, 1724, he applied, with three other members of the College of Physicians, for the keeping of the college garden, which had fallen into disuse. With the consent of the town council, the four physicians raised medicinal plants there and, in order to prepare drugs for the apothecaries' shops, set up a chemical laboratory at their own expense. Two years later Dr. Rutherford was appointed Professor of the Practice of Medicine in the medical school which he had helped to found. He used Boerhaave's "*Aphorismi de Cognoscendis et Curandis Morbis*" as a textbook, and for many years delivered clinical lectures in the Edinburgh Infirmary. He resigned in 1765, and died in 1779 at the age of eighty-four years (*6*), (*7*).

According to Florence MacCunn, both Sir Walter Scott and his mother inherited their "homely features and look of good-tempered shrewdness" from "old Dr. Rutherford, whose homely, heavy, sensible face hangs in the rooms of the Edinburgh College of Physicians" (*8*).

According to Lockhart, Dr. Daniel Rutherford "inherited much of the general accomplishments, as well as the professional reputation, of his father" (*9*). He was keenly interested in the classics, in English literature. and in mathematics, and his graduation thesis, like that of his celebrated

HERMANN BOERHAAVE, 1668–1738
Dutch physician, anatomist, chemist, and botanist. The Edinburgh Medical School was founded by pupils of Boerhaave while he was still in his prime. John Rutherford, father of Daniel Rutherford, was one of his devoted disciples.

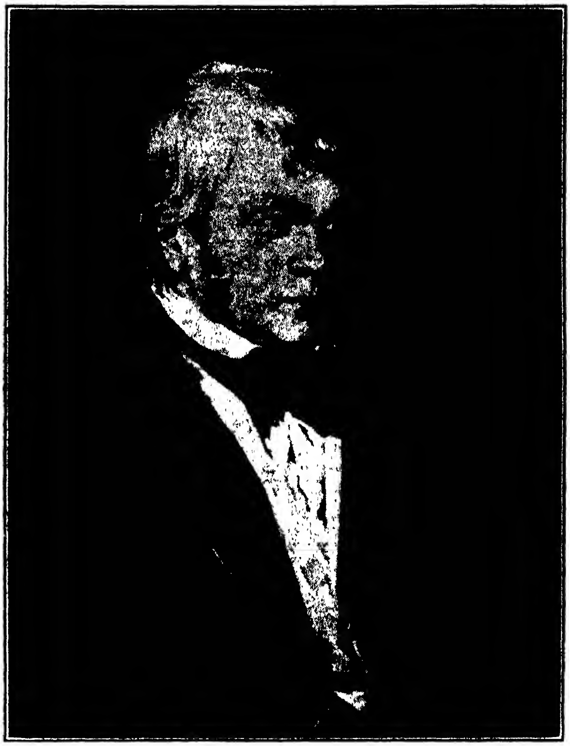
professor, Dr. Joseph Black, clearly revealed the existence of a new gas. Just as Black's dissertation, "*De humore acido a cibis orto, et magnesia alba,*"* published on June 11, 1754, had contained the discovery of carbon dioxide, Rutherford's thesis, "*Dissertatio inauguralis de aere fixo dicto, aut mephitico,*"† dated September 12, 1772, made clear the existence of nitrogen (phlogisticated air) as distinct from carbon dioxide (fixed air).

Although Stephen Hales had prepared nitrogen by absorbing the oxygen from a confined volume of atmospheric air, he had failed to recognize it as a new substance (*10*). Henry Cavendish was evidently the first person to distinguish nitrogen from other kinds of suffocating incombustible gases, but he had failed to publish his results. In a paper marked in his handwriting "communicated to Dr. Priestley," he had written:

> I am not certain what it is which Dr. P[riestley] means by mephitic air, though from some circumstances I guess that what he speaks of. . . was that to which Dr. Black has given the name of fixed air. The natural meaning of mephitic air is any air which suffocates animals (& this is what Dr. Priestley seems to mean by the words), but in all probability there are many kinds of air which possess this property. I am sure there are 2, namely, fixed air, & common air in which candles have burnt, or which has passed thro' the fire. Air which has passed thro' a charcoal fire contains a great deal of fixed air, which is generated from the charcoal, but it consists principally of common air, which has suffered a change in its nature from the fire. As I formerly made an experiment on this subject, which seems to contain some new circumstances, I will here set it down.

* The acid arising from food, and magnesia alba.

† Inaugural dissertation on the air called fixed or mephitic.



SIR WALTER SCOTT, 1771–1832

Scottish novelist and poet. His writings contain many interesting allusions to his uncle, Dr. Daniel Rutherford. Scott's circle of friends included Dr. William Hyde Wollaston, Sir David Brewster, Dr. John Davy, Sir Humphry Davy, and Joseph Black.

> I transferd some common air out of one receiver through burning charcoal into a 2nd receiver by means of a bent pipe, the middle of which was filled with powdered charcoal & heated red hot, both receivers being inverted into vessels of water, & the 2nd receiver being full of water, so that no air could get into it but what came out of the first receiver & passed through the charcoal. The quant. air driven out of the first receiver was 180 oz. measures, that driven into the 2nd receiver was 190 oz. measures. In order to see whether any of this was fixed air, some sope leys was mixed with the water in the bason, into which the mouth of this 2nd receiver was immersed; it was thereby reduced to 166 oz.,* so that 24 oz. meas. were absorbed by the sope leys, all of which we may conclude to be fixed air produced from the charcoal; therefore 14 oz. of common air were absorbed by the fumes of the burning charcoal, agreeable to what Dr. Hales and others have observed, that all burning bodies absorb air. . .*(11)*

With characteristic thoroughness Cavendish had passed the 166 ounces of residual air back again through fresh burning charcoal into another receiver. After another treatment with the soap lye there remained 162 ounces of a gas which he described as follows:

> The specific gravity of this air was found to differ very little from that of common air; of the two it seemed rather lighter. It extinguished flame, & rendered common air unfit for making bodies burn, in the same manner as fixed air, but in a less degree. . .*(11)*

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* The number 168 given in the British Association Reports is evidently a misprint.

In a paper read before the Royal Society in March, 1772 (six months before Dr. Rutherford's thesis was published), Priestley mentioned these experiments, but failed to record Cavendish's clear interpretation of them.

> The Honourable Mr. Cavendish favoured me [said he] with an account of some experiments of his, in which a quantity of common air was reduced from 180 to 162 ounce measures, by passing through a red-hot iron tube filled with the dust of charcoal. This diminution he ascribed to such a destruction of common air as Dr. Hales imagined to be the consequence of burning. Mr. Cavendish also observed, that there had been a generation of fixed air in this process, but that it was absorbed by sope leys(*12*).

In the same paper Priestley stated:

> Air thus diminished by the fumes of burning charcoal not only extinguishes flame, but is in the highest degree noxious to animals; it makes no effervescence with nitrous air, and is incapable of being diminished any farther by the fumes of more charcoal, by a mixture of iron filings and brimstone, or by any other cause of the diminution of air that I am acquainted with. This observation, which respects all other kinds of diminished air, proves that Dr. Hales was mistaken in his notion of the absorption of air in those circumstances in which he observed it. For he supposed that the remainder was, in all cases, of the same nature with that which had been absorbed, and that the operation of the same cause would not have failed to produce a farther diminution; whereas all my observations not only shew that air, which has once been fully diminished by any cause whatever, is not only incapable of any farther diminution, either from the same or from any other cause, but that it has likewise acquired new properties, most remarkably different from those which it had before, and that they are, in a great measure, the same in all the cases. . . .(*12*)

Priestley also observed that "lime-water never became turbid by the calcination of metals over it," and that "when this process was made in quicksilver, the air was diminished only one-fifth; and upon water being admitted to it, no more was absorbed" (*12*). He stated that this "air in which candles, or brimstone, had burned out. . . is rather lighter than common air" (*12*). Thus Priestley recognized, even at this early date, some of the most important properties of the gas now known as nitrogen.

Although the only copy of Rutherford's thesis which Sir William Ramsay was able to find is in the British Museum, Dr. Leonard Dobbin found a copy of it in the Edinburgh University Library and has published Crum Brown's English translation of it in the JOURNAL OF CHEMICAL EDUCATION (*40*). Although Ramsay stated in the first edition of "The Gases of the Atmosphere" that this dissertation "precedes Priestley's and Scheele's writings by a year or two," he corrected this in the second edition to read: ". . . Priestley had nearly anticipated Rutherford; and indeed, he speculated on the nature of the residual gas, left after combustion and absorption of the fixed air produced" (*13*). Although Rutherford referred in his thesis to Priestley's experiments on the effect of vegetation on the atmosphere, he was evidently unfamiliar with those on nitrogen (*14*), (*15*).

Dr. Black had noticed that when a carbonaceous substance is burned in air in such a manner that the fixed air can be absorbed in caustic alkali, a portion of the air remains. He had therefore assigned to his student, Daniel Rutherford, the investigation of this residual air in partial fulfillment of the requirements for the degree of doctor of medicine.

From Gentleman's Magazine, 1799

STEPHEN HALES, 1677–1761

British clergyman, biologist, chemist, and inventor. His most important researches were on blood pressure, circulation of sap, respiration, and ventilation.

The dissertation begins with an appropriate quotation from Lucretius and a review of the researches of Black and of Cavendish on fixed air. Rutherford then described his own experiments in which he had found that a mouse, left in a confined volume of atmospheric air until it died, had consumed $^1/_{16}$ of the air, and that treatment of the remaining air with alkali had caused it to lose one-eleventh of its volume. He found that the residual air extinguished the flame of a candle and that the wick would continue to glow in it for only a short time. He also discovered that air depleted by passage over ignited charcoal is identical with air vitiated by respiration. When he burned a metal, phosphorus, or sulfur in the atmosphere, however, he found that the residual gas contained no *mephitic air* [carbon dioxide], but that it had undergone "a singular change" (*14*). After burning a candle or suffocating a mouse in a confined volume of air, and absorbing the resulting *fixed air*, or carbon dioxide, in caustic alkali, Rutherford concluded from careful study of the residual gas that

> . . .healthy and pure air by being respired, not only becomes partly mephitic [poisonous], but also suffers another change in its nature. For after all *mephitic air* [carbon dioxide] is separated and removed from it by means of a caustic lixivium, that which remains does not thence become more healthful; for although it makes no precipitate of lime from water, yet it extinguishes fire and life no less than before (*16*).

Rutherford also believed that "pure air is not converted into mephitic air by force of combustion, but that this air rather takes its rise or is thrown out from the body thus resolved" (*15*). He concluded, in other words, "that that unwholesome air is composed of atmospheric air in union with, and, so to say, saturated with, phlogiston" (*15*). After pointing out the distinction between this new "noxious air" [nitrogen] and "mephitic air" [carbon dioxide], the air evolved by the action of acids on metals, and the air from decaying flesh, Rutherford added that he was unable to state with certainty anything regarding the composition of mephitic air nor to explain its inability to support life. He believed, however, that it was possibly generated from the food, and expelled as a waste product from the blood by means of the lungs (*14*).

> Certain experiments [said he] appear to show. . .that it consists of atmospheric air in union with phlogistic material: for it is never produced except from bodies which abound in inflammable parts; the phlogiston ever appears to be taken up by other bodies, and is hence of value in reducing the calces of metals. I say from phlogistic material, because as already mentioned, pure phlogiston, in combination with common air, can be seen to yield another kind of air. . .(*15*)

Sir William Ramsay believed that Rutherford "may well be credited with the discovery of nitrogen" and that his thesis on mephitic air "was an advance, though not a great one, in the development of the theory of the true nature of air" (*15*). B. B. Woodward believed, however, that "all the facts and views recorded by Rutherford are to be found in Priestley's memoir published in the *Philosophical Transactions* for 1772 (p. 230 *et passim*), and read six months before the publication of Rutherford's tract; but Priestley's exposition is less methodical and precise" (*14*). Both Rutherford and Priestley believed the new gas to be atmospheric air saturated with phlogiston, and neither of them regarded it as an element (*14*).

In his "Lectures on the Elements of Chemistry," Dr. Joseph Black made the following statement about the discovery of nitrogen:

> Scarcely inferior to vital air in importance is the *faul air* of Dr. Scheele, which I mentioned on the same occasion, as that noxious portion of atmospherical air which remains when the vital air has been absorbed by the *hepar sulphuris* [product of heating potassium carbonate with sulfur] (*17*). I must here observe, that this portion of our atmosphere was first observed in 1772 by my colleague Dr. Rutherford, and published by him in his inaugural dissertation. He had then

> discovered that we were mistaken in supposing that all noxious air was the fixed air which I had discovered. He says, that after this has been removed by caustic alkali or lime, a very large proportion of the air remains, which extinguishes life and flame in an instant. Soon after this Dr. Priestley met with this noxious air, which was produced in a variety of experiments, in which bodies were burned, or putrefied, or thickened in certain cases, or metals calcined, or minerals effloresced, &c.&c. In all these cases, he thought that he had reason to believe that phlogiston had quitted the substances under consideration—had combined with the air,—and had thus vitiated it. Now saturated with phlogiston, the air could take no more, and therefore extinguished flame. He called all these processes *phlogisticating processes*, and the air thus tainted *phlogisticated air* (*18*).

According to Dr. Black, it was Scheele who proved that the diminution of bulk which accompanied the vitiation of the air by these combustion processes

> . . .was owing to a real abstraction of all the vital air which the atmospheric air contained. For when any of these "*phlogisticating processes*" of Dr. Priestley were performed in vital air, it was *totally* absorbed (*19*). The remainder therefore, when the experiment was made in common air, was considered by him as a primitive air, unchanged in its properties. He called it *faul air*, which may mean either *rotten* air, because it is produced in vast abundance by putrefying bodies, or simply *foul air*, *i. e.*, tainted occasionally, when the phlogiston is more than will saturate the vital air.

Dr. Black also mentioned Berthollet's preparation of nitrogen by pouring nitric acid on fresh muscle fiber and Fourcroy's discovery of this gas in the swimming bladders of carp, bream, and other fish (*20*). He said that, although the discoverers of the element had called it by various names—*phlogisticated*, *foul*, or *mephitic air*, or *choke-damp* (*Stickstoff*)—the name *nitrogen* had been suggested by "Mr. Chaptal and other chemists of the first rank," after Cavendish had prepared niter by sparking the new gas with oxygen in presence of caustic potash (*21*). The French name *azote* was suggested by Lavoisier because of the inability of the gas to support life (*18*), (*22*), (*23*), (*24*). Although Lavoisier (*25*) had mentioned nitrogen in his list of elements, Sir Humphry Davy doubted its elementary nature as late as 1808–09 and attempted to decompose it (*26*).

After his graduation, young Dr. Rutherford studied in Paris, Italy, and London for three years before returning to Edinburgh to practice medicine. During his stay in Paris, he declined an invitation to a party at which Prince Charles Edward was expected, saying that, out of respect for the honor of a fallen house, he wished to avoid the spectacle of seeing the prince intoxicated (*1*).

Since Max Speter (*27*), (*41*) mentioned that John Mayow in his "*Tractatus Quinque*" anticipated Lavoisier (*28*) in the belief that all acids contain

From Kay's Portraits

JOHN HOPE, 1725–1786

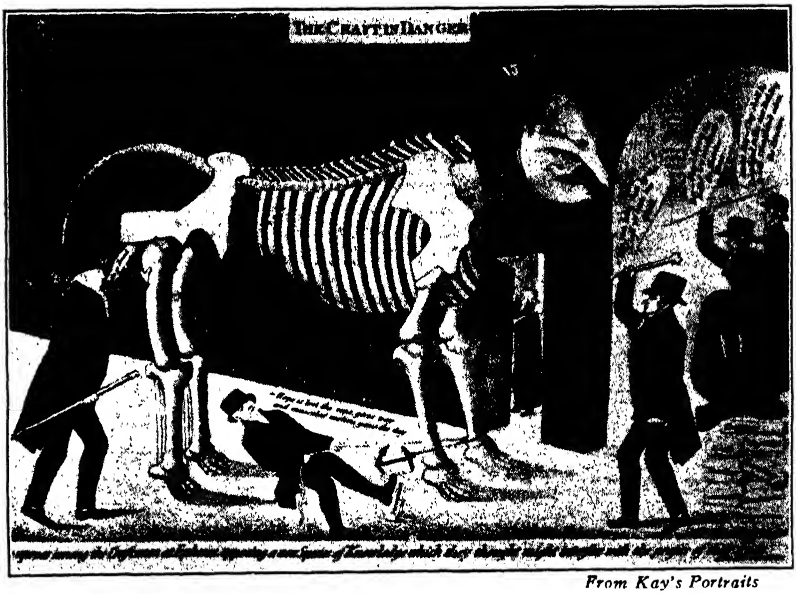
Predecessor of Daniel Rutherford as professor of botany and *materia medica* at the University of Edinburgh. Dr. Hope had the plants in the Botanical Garden arranged according to the Linnæan system. In the above portrait he is shown instructing one of the workmen. His son, Thomas Charles Hope (1766–1844), was Rutherford's contemporary as professor of chemistry at Edinburgh.

oxygen, it is interesting to know that Dr. Rutherford also made the same error. A note by John Robison in his edition of Black's "*Lectures on the Elements of Chemistry*" reads as follows:

> I cannot omit mentioning in this place, that my colleague, Dr. Daniel Rutherford read, in the year 1775, to the Philosophical Society of Edinburgh, a dissertation on nitre and nitrous acid, in which this doctrine is more than hinted at or surmised. By a series of judiciously contrived experiments, he obtained a great quantity of vital air from nitric acid; about one-third of that quantity from the sulphuric acid, as contained in alum; and a small quantity (and this very variable and uncertain) from the muriatic acid. The manner in which it came off from the compounds, in various circumstances, led him to think that the different quantities obtained did not arise from the different proportions in which it was contained in those acids, but merely in the different forces with which it was retained. He therefore concluded that vital air was contained in all acids, and thought it likely that it was a *necessary* ingredient of an acid; and seeing that it was the *only* substance found, as yet, in them all, he thought it not unlikely that it was *by this that they were acid*, and he points out a course of experiments which seems adapted to the decision of this question. I was appointed to make a report on this

> dissertation; and I recollect stating as an objection to Dr. Rutherford's opinion, "that it would lay him under the necessity of supposing that vitriolic acid was a compound of sulphur and vital air," which I could not but think an absurdity. So near were we at that time to the knowledge of the nature of the acids (*29*).

Mayow's "*Tractatus Quinque*" was published in 1674, Dr. Rutherford's communication was read in 1775, and Lavoisier's statement that oxygen is an essential constituent of all acids is contained in a paper read on November 23, 1779.



From Kay's Portraits

CARTOON SHOWING A CONTROVERSY IN 1817 OVER THE FOUNDING OF A CHAIR OF COMPARATIVE ANATOMY

The candidate, Dr. Barclay, is shown astride the elephant's skeleton. His opponent, Dr. Thomas Charles Hope (center foreground), has his anchor firmly grounded in "the strontian." This is an allusion to the research in which he distinguished between baryta and strontia. The scene is laid at the entrance to the old College of Edinburgh.

In 1786 Rutherford was appointed successor to John Hope, the professor of botany at the University of Edinburgh, and in the same year he was married to Harriet Mitchelson of Middleton (*1*). With pardonable family pride, Sir Walter Scott once said that Dr. Rutherford "ought to have had the chemistry class, as he was one of the best chemists in Europe; but superior interest assigned it to another, who, though a neat experimentalist, is not to be compared to poor Daniel for originality of genius. . ." (*30*). Bower's "*History of the University of Edinburgh*" states that the discovery of nitrogen "entitles Rutherford to rank very high among the chemical philosophers of modern times" and that "the reputation of his discovery being speedily spread through Europe, his character as a chemist of the first eminence was firmly established, and much was augured from a young man in his twenty-second year having distinguished himself so remarkably" (*30*).

Sir R. Christison, one of Dr. Rutherford's botany students, said, on the other hand,

> Tradition had it in my student years that he was disappointed at not being made assistant and successor to Black in 1795, when that office was given to Dr. Charles Hope; and he again, son of the botanical predecessor of Rutherford, was said to have preferred to step into his own father's University shoes rather than into those of Dr. Black. However that may have been, Hope highly distinguished himself in his Chemical Chair; while Rutherford, in that of Botany, which he filled for thirty-four years, always seemed to lecture with a grudge, and never contributed a single investigation to the progress of the science which he taught. . .His lectures, however, were extremely clear, and full of condensed information, his style was beautiful, and his pronunciation pure and scarcely Scotch (*31*).

Because of hereditary gout, Dr. Rutherford was unable to take his botany students on field trips, and Sir R. Christison thought that that important duty ought to have been entrusted to the head gardener (*31*).

I. B. Balfour also thought it strange that Dr. Rutherford should have been chosen to teach botany, and stated in the "Makers of British Botany" that "Rutherford was a chemist, and I have not discovered in any references to him expressions that he was at this period of his life interested in plants otherwise than as objects for his experiments in relation to the chemistry of the atmosphere" (*32*). Nevertheless, the botanical garden developed under Rutherford's administration into one of the best in the world, and the plants of Scotland were carefully recorded by the head gardeners (*32*).

Dr. Rutherford was a fellow of the Philosophical (later the Royal) Society of Edinburgh, and contributed to its *Transactions* a description of a thermometer for reading maximum and minimum temperatures (*33*), (*34*). The portion of the instrument designed for reading minimum temperatures is a horizontal tube filled with alcohol in which is immersed a small glass rod with a knob at each end. As long as the temperature keeps falling, the concave surface tension film of the alcohol drags this little rod back with it, but when the temperature rises, the expanding alcohol moves past the rod, leaving it stationary. The portion of the thermometer used for reading maximum temperatures consists of a horizontal tube containing a thread of mercury which pushes a small bar of iron ahead of it as long as the temperature keeps rising (*34*). Dr. Rutherford also made experiments to improve the air pump (*33*).

He published an octavo volume called "*Characteres Generum Plantarum,*" and collaborated with James Hamilton and James Gregory in writing "*A Guide for Gentlemen Studying Medicine at the University of Edinburgh*" (*14*). He was a member of the Linnæan Society and of the Aesculapian, Harveian, and Gymnastic Clubs (*14*).

Dr. and Mrs. Rutherford had two sons and three daughters, but in 1805 the elder son, John, a boy of seventeen, was lost in the shipwreck of an East Indiaman commanded by John Wordsworth, a brother of the famous poet. After his words of sympathy to Wordsworth, Scott wrote, " . . . The same dreadful catastrophe deprived me of a near relation, a delightful and promising youth, the hope and pride of his parents. He had just obtained a cadetship, and parted from us all in the ardor of youthful hope and expectation, leaving his father (a brother of my mother) almost heartbroken at his departure. . ." (*35*). Fourteen years later Scott said, when writing to his son at the time of Dr. Rutherford's death, "Since you knew him, his health was broken and his spirits dejected, which may be traced to the loss of his eldest son. . . ." (*30*).

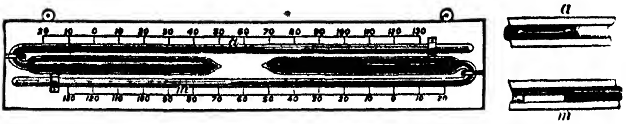
Scott's correspondence with his aunt, Miss Christian Rutherford, shows that he found in his uncle's family ". . . more than one kind and strenuous encourager of his early literary tastes." Nevertheless, his youthful habit of reading at breakfast often brought forth good-natured protest from the doctor (*9*).

In December, 1819, Scott suffered the tragic loss of three of his nearest relatives within scarcely more than a week (*30*), (*36*). On the twelfth, his mother, who had been in excellent health and spirits in spite of her advanced age of eighty-seven years, was suddenly stricken with such a severe attack of paralysis that Dr. Daniel Rutherford felt certain that she could not live more than a few days.

> But [said Scott in a letter to his brother in Canada], "this heavy calamity was only the commencement of our family losses. Dr. [Daniel] Rutherford, who had seemed perfectly well and had visited my mother upon Tuesday the fourteenth, was suddenly affected with gout in his stomach, or some disease equally rapid, on Wednesday the fifteenth, and without a moment's warning or complaint, fell down a dead man, almost without a single groan. You are aware of his fondness for animals; he was just stroking his cat after eating his breakfast, as usual, when, without more warning than a half-uttered exclamation, he sunk on the ground, and died in the arms of his daughter Anne. Though the Doctor had no formed complaint, yet I have thought him looking poorly for some months; and though there was no failure whatever in intellect, or anything which approached it, yet his memory was not so good, and I thought he paused during the last time he attended me, and had difficulty in recollecting the precise terms of his recipe. Certainly there was a great decay of outward strength.
>
> We were very anxious about the effect this fatal news was likely to

> produce on the mind and decayed health of our aunt, Miss C. Rutherford, and resolved, as her health had been gradually falling off ever since she returned from Abbotsford, that she should never learn anything of it until it was impossible to conceal it longer. But God had so ordained it that she was never to know the loss she had sustained. and which she would have felt so deeply. On Friday the 17th December, the second day after her brother's death, she expired, without a groan and without suffering, about six in the morning. . .It is a most uncommon and afflicting circumstance, that a brother and two sisters should be taken ill the same day—that two of them should die without any rational possibility of the survivance of the third—and that no one of the three could be affected by learning the loss of the other. The Doctor was buried on Monday 20th, and Miss Rutherford this day (Wednesday 22nd), in the burial-place adjoining to and surrounding one of the new Episcopal chapels [St. John's Chapel], where Robert Rutherford [son to the professor of botany] had purchased burial-ground of some extent. . .and in this new place I intend to lay our poor mother when the scene shall close. . .(*37*).

Scott once paid the following tribute to his uncle: "Dr. Rutherford was a very ingenious as well as an excellent man, more of a gentleman than those of his profession too often are, for he could not take the back-stairs mode of rising in it, otherwise he might have been much more wealthy. . ." (*30*). This kindly Scottish physician is remembered today for his maximum and minimum thermometer and for the brilliant research in which he clearly distinguished between carbon dioxide and nitrogen (*38*), (*39*).



RUTHERFORD'S MAXIMUM AND MINIMUM THERMOMETER
a. . .Index of minimum thermometer.
m. . .Index of maximum thermometer.

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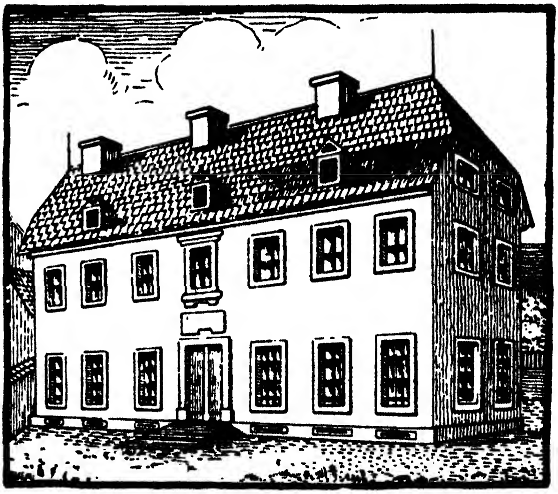
VII. CHROMIUM, MOLYBDENUM, TUNGSTEN, AND URANIUM

The publications and correspondence of Bergman and Scheele contain interesting allusions to the d'Elhuyar brothers, to Hjelm, and to the early history of the metals tungsten and molybdenum which they discovered. The presence of a new metal in pitchblende was recognized by Klaproth in 1789, but it remained for Peligot half a century later to isolate uranium. Chromium, now the most familiar element of the group, was the last to be discovered when the immortal French chemist Vauquelin finally isolated it in 1798 from a Siberian mineral. For further information about tungsten see pp. 143–56.

. . . . . .

> *"Les laboratoires sont les temples de l'avenir, de la richesse et du bien-être; c'est là que l'humanité grandit, se fortifie et devient meilleure." (1)**

During the last two decades of the eighteenth century, investigations were made which foreshadowed the discovery of chromium, molybdenum, tungsten, uranium, tellurium, chlorine, titanium, and beryllium; but some of these elements were not actually isolated until much later. For the sake of simplicity, only the closely related elements, tungsten, molybdenum, uranium, and chromium will be considered in this chapter.



LAMPADIUS' LABORATORY AT FREIBERG, 1800

Many of the most eminent mineralogical chemists in Europe were educated at the Freiberg School of Mines. The d'Elhuyar brothers, who discovered tungsten, and A. M. del Río, who discovered vanadium ("erythronium"), received part of their training there, and F. Reich and H. T. Richter, the discoverers of indium, and Clemens Winkler, the discoverer of germanium, were members of the teaching staff.

Tungsten

Tungsten and tungstic acid were first recognized in the minerals wolframite and scheelite. As early as 1761, J. G. Lehmann analyzed the former, without recognizing, however, that it contained two metals which were then unknown, tungsten and manganese. When he fused it with sodium nitrate and dissolved the melt

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* "Laboratories are the temples of the future, of wealth, and of welfare; in them humanity grows greater, stronger, and better."

in water, he obtained a green solution which became red (sodium manganate and permanganate). Addition of a mineral acid caused the precipitation of a soft, spongy, white earth (tungstic acid) which, after long standing in contact with the solution, became yellow. He concluded, however, that the wolframite from Zinnwald must be "a mineral consisting mainly of a glassy earth, much iron, and a trace of zinc" and that it is related to a mineral used by glassmakers, "*magnesia vitriariorum*," or pyrolusite (*58*).

In 1779 Peter Woulfe examined this mineral and concluded that it must contain something new. "The Spar of the Germans," said he, "is commonly called white tin ore .... This is supposed by several to be rich in tin; but the Saxon mineralogists assert that it contains none. The only experiment I made with it was to digest it in a powdered state with acids, by which means it acquires a rich yellow colour, like turbith mineral [basic mercuric sulfate]; the acid of salt answers best for this experiment. This is the only substance I know of which has this property" (*65*).

There is found in Sweden a white mineral which used to be called *tungsten*, or *heavy stone*, and which is now known as scheelite (*20*). In 1781 Scheele gave the following description of it: "The constituents of this variety of stone seem probably to be still unknown to chemists. Cronstedt enumerates it amongst the ferruginous varieties of stone, under the name of *Ferrum calciforme, terra quadam incognita intime mixtum*. That which I used for my experiments is pearl-coloured and taken from the iron mine of Bitsberg" (*56*). He decomposed the mineral with aqua fortis (nitric acid) and found that it contained lime and a white acidic powder similar to molybdic acid but differing from it in the following respects:

"(1) The acid of molybdaena is volatile and melts in the fire, which does not occur with acid of tungsten. (2) The first-named acid has a stronger affinity for phlogiston, which is seen from its union with sulphur and the change it undergoes on calcination with oil. (3) *Calx molybdaenata* does not become yellow with acid of nitre and is dissolved by it quite easily. With tungsten the contrary occurs. (4) *Terra ponderosa molybdaenata* is soluble in water, but not the same variety of earth united with our acid; and (5) acid of molybdaena has a weaker attraction for lime than our acid" (*56*).

Thinking, because of its high specific gravity, that scheelite might contain the alkaline earth baryta, Torbern Bergman analyzed it, but found instead an *acidic* oxide (tungstic acid). In 1781 he concluded that both tungstic and molybdic acids must be related to white arsenic and that therefore it ought to be possible to prepare metals from them. Since Bergman himself could not find time to test this hypothesis, he expressed the hope that someone else would make the necessary experiments (*57*).

In the meantime two Spanish chemists, the d'Elhuyar* brothers, found

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* The name was also spelled Luyarte, de Luyart, and d'Elhuyart. In Spanish books it is spelled *de Elhuyar*. The brothers themselves did not agree as to the spelling.

in wolfram, a dark brown mineral (wolframite) then supposed to be an ore of tin and iron, an acid (wolframic) which they found to be identical with tungstic acid (*2*), (*21*), (*25*), (*37*), (*38*).

Don Fausto d'Elhuyar was born in 1755 at Logroño, Spain. With his brother, Don Juan José, he went to Freiberg to study chemistry and mineralogy at the School of Mines, and Don Juan José later went to Upsala to work for half a year in Bergman's famous laboratory (*21*), (*41*). The Swedish professor mentioned him in his diary. "Mr. de Luyarte, from Spain," said he, "came with Mr. de Virly to Upsala on the same errand [to study], where they not only privately went through an entire course in higher chemistry, but also, with others, went to private lectures in assaying, each passing excellent tests. They remained until the end of the term" (*27*), (*39*).

In a letter to Bergman dated July 5, 1782, Scheele mentioned a visit which these chemistry students had recently paid him: ". . . The foreign gentlemen," he said, "stayed with me two days; I found real pleasure in talking with them about chemical matters; moreover they were not inexperienced in that field" (*3*).

From Nordenskiöld's "Carl Wilhelm Scheele. Nachgelassene Briefe und Aufzeichnungen"

BÖRJESON'S STATUE OF CARL WILHELM SCHEELE

Scheele discovered tungstic and molybdic acids, and was the first to distinguish between graphite and molybdenite.

In 1783 the brothers collaborated in a research on tungsten and wolfram, and found that both these ores contained the tungstic acid that Scheele had reported. The first metallic tungsten was prepared not from scheelite but from wolframite (*spuma lupi*) from Zinnwald. "We know no Spanish name for this mineral," wrote the d' Elhuyar brothers in

1783, "nor do we know that it has been found in our country" (*58*). The possibility of obtaining a new metal by reducing tungstic acid had already been suggested by Bergman and Scheele. The apparatus used by the d'Elhuyar brothers was very simple. An intimate mixture of tungstic acid and powdered charcoal was heated strongly in a luted crucible (*22*). After cooling the crucible, they removed from it a dark brown, metallic button, which crumbled easily in their fingers, and when they examined the powder with a lens, they saw metallic globules of tungsten, some of which were as large as the head of a pin (*2*), (*26*). On April 2, 1784, Scheele wrote to Bergman, "I am glad that Mr. Luyarte has obtained a tungsten regulus. I hope he has sent you specimens of it" (*4*).

Courtesy Dr. Moles and Mr. de Gálvez-Cañero

FAUSTO DE ELHUYAR

President of the Mining Tribunal and Director General of Mines of New Spain. For more than thirty years he directed the College of Mines of Mexico.

The d'Elhuyar brothers afterward went to America and in 1788 Fausto became Director of Mines of Mexico. Don Juan José died in Bogotá, Colombia, but at the outbreak of the Revolution Don Fausto returned to Spain. His reason for leaving Mexico may be inferred from the note found at the end of one of Andrés del Rio's papers:

> The preceding analysis only too plainly shows the wretched state of our laboratory in Mexico, after having been for thirty years under the direction of so distinguished a chemist as M. Elhuyar, the discoverer of wolfram and cerium[!] It is true that under the old government, this savant found himself obliged to become a man of business, undoubtedly much against his inclination; for it is impossible that he who has once imbibed a taste for science can ever abandon it (*5*).

After returning to Spain Fausto served on the General Council of Public Credit, was made Director General of Mines, drew up the famous mining law of 1825, and planned the School of Mines of Madrid. After a long, eventful, and useful life, he died in Madrid on January 6, 1833 (*6*).

In 1785 Rudolf Erich Raspe, author of "The Adventures of Baron Münchausen," showed that the metal obtained from scheelite is identical with that from wolframite and that it hardens steel (*59*). In an investigation of two refractory specimens of scheelite, he succeeded in reducing them to a "regulus which contains only a little iron and is unusually hard, strong, and refractory. It cuts glass like good hardened steel and is therefore well suited for the manufacture of all kinds of hard tools, for the improvement of several iron- and steel manufactures, even perhaps for the pouring of anchors in a single operation." He also prepared a fine yellow pigment from the mineral.

When he compared a regulus from wolframite with one from scheelite, he found that the former contained more iron and that "it has almost the same color as the scheelite regulus and is, if I be not mistaken, one and the same thing. Only yesterday I began the experiments with wolframite, which I regard as a kind of crystallized scheelite and which, according to a report in the newspapers, Don Luyarte [de Elhuyar] and another Spaniard have recently announced as containing a new metal" (*59*). J. Hawkins said that Raspe obtained his wolframite from "Poldice" [Poldise], Cornwall and his scheelite from Entral (*60*). Wolframite is now known to be a ferrous manganous tungstate of the composition $(Fe, Mn)WO_4$; scheelite is calcium tungstate, $CaWO_4$.

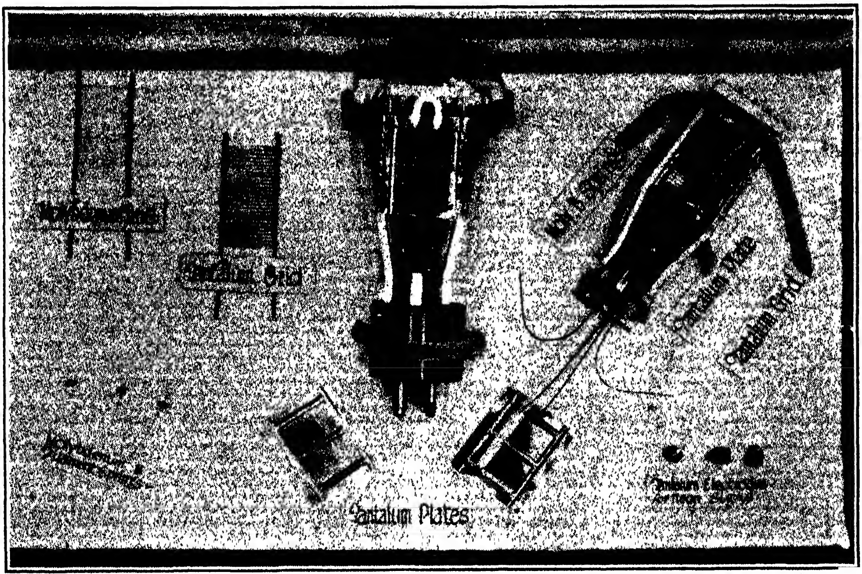
Rudolf Erich Raspe was born in 1737 in Hanover and educated in the natural sciences and philology at Göttingen and Leipzig. Benjamin Franklin met both Raspe and Baron von Münchausen on his visit in Hanover (*61*). Raspe was brilliant and versatile, but extravagant and dishonest. After he had pawned some valuable medals which he had stolen from the museum at Cassel, the police described him as a red-haired man, attired alternately in a gold-embroidered red suit, and suits of black, blue, and gray. After his arrest at Clausthal, he escaped in the night and embarked for England, where for the rest of his life he earned his living by tutoring and translating. He was also employed for a time in the mines of Cornwall and Ireland. He died at Mucross, Ireland, in 1794 (*62*).

As late as 1800, F. C. Gren wrote: "It is still questionable whether the oxyd of wolfram is reducible to a reguline metal. No chemist has yet succeeded in obtaining a pure regulus of it, at least of some magnitude. Whenever the experiment was attempted, the result, upon examination with the glass, was always found to be a mere congeries of small metallic globules" (*63*).

Nicholson's Journal for the same year contained a brief account of Guyton-Morveau's attempt to fuse tungsten: "Guyton, in a fire urged by the blast of three pipes to 185 degrees of the pyrometer, obtained a well rounded piece of 35 grammes. But it broke in the vice, and exhibited a central portion, which was only agglutinated, and soon acquired a purple colour by exposure to the air . . . and he concludes from the infusibility and brittleness of this metal that it affords little promise of utility in the arts, except in metallic alloys, or by virtue of the property which its oxide possesses, of affording fixed colours, or giving fixity to the colours of vegetables" (*64*). The tungsten lamp filaments, tungsten contact points, and high-speed steel so indispensable to modern life have all resulted nevertheless from the great discovery made so long ago by the d' Elhuyar brothers in Spain.

Molybdenum

Native molybdenum disulfide is a soft, black mineral that looks much like graphite. In fact, until the latter part of the eighteenth century, both were sold under the same name: *Molybdän*, or *molybdenum*. German writers used to call molybdenite "Wasserbley," a name suggestive of lead. Although Johann Heinrich Pott knew that it is not a lead mineral, he confused it with graphite, "Reissbley," and believed that it consisted of lime, iron, and sulfuric acid (*50*).



Courtesy Fansteel Products Co., Inc.

Vacuum Tube Showing the Use of Tantalum and Molybdenum

In 1754 Bengt (Andersson) Qvist, a friend of A. F. Cronstedt and Sven Rinman, investigated a mineral which he described as follows: "At one locality of the Bispberg there is found a light, roughly pointed, loose, glistening molybdenite (Wasserblei) consisting of flexible lamellae which are not firmly coherent and which for the most part succeed one another in the form of regular pyramids.... In the muffle it gave off dense black fumes and a suffocating sulfurous odor; at the same time appeared small yellow "flowers" like snowflakes, which crystallized in masses of rather elastic filaments or lamellae" (*51*).

Qvist observed that the calx was yellow while hot but glistening white when cold. He obtained positive tests for iron and copper, and found that "on digestion, it gave no sweetness to distilled vinegar" (an indication that molybdenite is not a lead mineral). In one specimen from England he detected tin. He concluded that "it is evident from several experiments that the molybdenite itself contains something specifically metallic in addition to those just mentioned" (*51*).

On December 19, 1777, Scheele wrote to J. G. Gahn: "You doubtless have there in your mineral collection some foliated *molybdaena* like the enclosed sample. I received some in the summer from Assessor Hoffgaard; I find something peculiar in it. Please be so good as to send me a little of it by mail. On some better occasion I shall describe my experiments" (*52*).

Scheele kept this promise, and on May 15th of the following year wrote Gahn as follows: "I now have the pleasure of giving you a short report of my experiments with *molybdaena*. Professor Bergman, Assessor Rinman, and B. Hermelin [Samuel Gustav Hermelin] all sent me some of it" (*52*).

In 1778 Scheele published his analysis of the so-called "lead ore" (molybdenite), then known as *molybdaena*. "I do not mean the ordinary lead ore," said he, "that is met with in the apothecaries' shops, for this is very different from that concerning which I now wish to communicate my experiments to the Royal Academy. I mean here that which in Cronstedt's Mineralogy is called *molybdaena membranacea nitens* and with which Qvist and others probably made their experiments. The kinds I had occasion to submit to tests were got in different places, but they were all found to be of the same nature and composed of the same constituents" (*53*).

Because of its softness, Scheele had to devise an ingenious method of pulverizing the mineral. "Now since it does not permit of being ground to fine powder by itself, on account of its flexible lamellae, some fragments of vitriolated tartar [potassium sulfate] were also placed in the glass mortar occasionally, when it was at last transformed to a fine powder" (*53*). Scheele then washed the powder by decantation with hot water to remove the potassium sulfate. By adding nitric acid to the mineral several times and evaporating to dryness, he succeeded in decomposing it so completely that only a white powder remained, which he named *terra molybdaenae*.

Bengt Qvist had already shown that the mineral is volatile in the open fire and that it contains sulfur, and Scheele found that "earth of molybdaena is of an acid nature." He examined it "by the method of reduction with black flux and charcoal and with glass of borax and charcoal, but it was in vain; I did not perceive anything in the least metallic" (*53*). Scheele showed that graphite and the molybdenum mineral are two entirely different substances. Although nitric acid has no effect on graphite, it reacts with the mineral "molybdenum," or molybdenite, to give sulfuric acid and a peculiar white solid, which he named molybdic acid (*2*), (*23*). Bergman suggested to Scheele that molybdic acid must be the oxide of a new metal, and since the latter chemist did not have a furnace suitable for the purpose, he asked his friend Hjelm to attempt the reduction of the ore (*7*).

Peter Jacob Hjelm was of about the same age as Scheele, for he was born on October 2, 1746, at Sunnerbo Härad. He probably met the latter in Upsala, for their correspondence began shortly before Scheele went to Köping (*7*). At Scheele's suggestion he tried to reduce molybdic acid with carbon, and in order to get very intimate contact between the two reagents, he stirred the pulverized acid with linseed oil to form a paste. When he heated the mixture strongly in a closed crucible, the oil became carbonized, and the carbon reduced the molybdic acid to the metal, which became known as molybdenum (*2*), (*24*).

On November 16, 1781, Scheele wrote to Hjelm,

> . . . I gladly excuse your delay in writing, for I know you are now very busy. I rejoice that we now have another new half-metal, molybdaenum. I think I can already see the French seeking to deny the existence of this new half-metal, since they are not the discoverers of it. . . The acidum enclosed in paper is the same acid that I fused in a crucible. If you prepare a regulus from it, I beg you, because of its rarity, to send me some of it, even if it is only a grain. I have no molybdaenum (*8*).

In another of his letters to Hjelm he said, "As far as I can judge of your work, it does you all credit" (*9*).

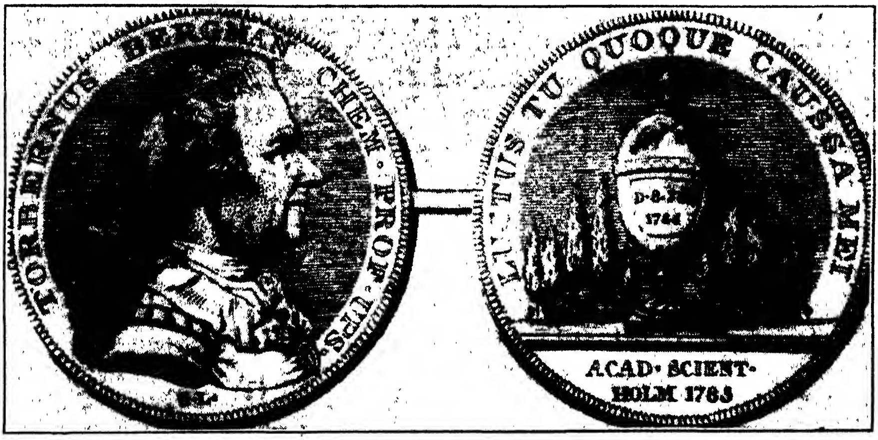
Although this correspondence shows that Hjelm must have isolated molybdenum as early as the fall of 1781, his first paper on it was not published until much later. In 1790, after both Scheele and Bergman had died, he wrote:

"At the request of the late Scheele and Bergman, I tried to prepare a metal from yellow molybdic acid, using the same acid which the former himself sent me. I first fused ox blood several times with the vegetable alkali: then, when I wanted to reduce the acid, I added to it an equal amount of microcosmic salt, and a little tartar or black flux from which I had often smoked off some grease. I placed the entire mixture, sometimes also covered with common salt, in a luted crucible, and exposed it for several hours to the heat of a good wind furnace. If one wishes to reduce a new portion of acid again, one uses the glass produced in the foregoing operation, as it might then be less inclined to attack the earth of molybdenum itself and to dissolve it.

"The small regulus I obtained from the meager supply of earth brought forth the description of it to be found in Herr Bergman's paper on the blowpipe. The traces of sulfur and iron present in the reguluses I attribute to the molybdic earth which I received, for my fluxes were perfectly pure; the former were therefore only a kind of crude metal in which, however, the metallic nature is fundamental. Several writers, including Herr [Bertrand] Pelletier, Sage, Ilsemann, and Heyer, assume this: yet they have not engaged in the actual reduction" (*42*).

Hjelm prepared purified molybdic acid and a pure regulus, which he examined with the microscope. In an unsuccessful attempt to fuse the molybdenum, he raised the temperature of the wind-furnace with "fire-air" (oxygen) obtained by adding two pounds of crude pyrolusite to the fire (*24*).

He published papers on the composition of coal, wood, charcoal, steel, pyrolusite, molybdenite, and spring waters, on the arts of purifying lead, hardening copper, and burning bricks, on the working of saltpeter and indigo, on resuscitation of patients with suspended animation, and on the porphyry industry at Elfdal, East Dalarne (*54*).



TORBERN OLOF BERGMAN, 1735–1784

Swedish chemist, pharmacist, and physicist. He was among the first to investigate the compounds of manganese, cobalt, nickel, tungsten, and molybdenum.

In 1782 Hjelm was made Assay Master of the Royal Mint at Stockholm, and twelve years later he became Director of the Chemistry Laboratory at the Bureau of Mines. He died in that city on October 7, 1813 (*7*).

Edward Daniel Clarke, who visited him in 1799, described him as "a most intelligent man and very able chemist, of the name of Hjelm, who permitted us to see the collection of minerals belonging to the Crown . . . . Mr. Hjelm was employed, at the time of our arrival, in making what he called Spa Water; that is to say, water impregnated with carbonic acid gas; by the usual process of agitating the fluid in a receiver containing the gas collected from the effervescence of limestone when exposed to the action of an acid. Mr. Hjelm used the sulphuric acid and powdered marble. He showed to us a very great chemical curiosity; namely, a mass of chromium in the metallic state, nearly as large as the top of a man's thumb. We could perceive, however, that the Swedish chemists, celebrated as they justly are, carry on their works in the large way: the furnaces used by Mr. Hjelm, in the Royal Laboratory, were of the size of those in our common blacksmiths' shops; and the rest of his apparatus was on a similar scale" (*55*).

Professor Hjelm was one of Scheele's best friends, and their correspondence is still treasured by the Stockholm Academy of Sciences. In his later days Hjelm kept a complete diary, which is now in possession of the Royal Library at Stockholm (*7*). When Scheele wrote to Hjelm, "*Es ist ja nur die Wahrheit, welche wir wissen wollen, und welch ein herrliches Gefühl ist es nicht, sie erforscht zu haben*"* (*10*), he knew that he was expressing the latter's feelings as well as his own.

In 1785 B. Pelletier proved that the ore mineralogists used to call "molybdenum" is a sulfide of that metal (*28*). The molybdic acid obtained by Scheele does not exist as such in the mineral, but was produced when he oxidized the molybdenum sulfide with nitric acid.

Molybdenum is a much softer, more ductile metal than tungsten, and is indispensable for the filaments, grids, and screens required in radio broadcasting. Hence this great modern industry rests upon the researches that gave so much intellectual pleasure to Hjelm and Scheele.

Uranium

The early history of uranium is closely associated with the name of Martin Heinrich Klaproth, a German chemist who was born in Wernigerode in the Harz on December 1, 1743. When he was eight years old, the family became impoverished by a serious fire. Since there was little money left for the education of the three Klaproth boys, little Martin Heinrich earned his tuition by singing in the church choir. After receiving a little instruction in Latin at Wernigerode, he was apprenticed at the age of sixteen years to an apothecary. After five years of apprenticeship, he worked for four years in public laboratories at Quedlinburg and at Hanover, and at Easter time in 1768 he became an assistant in Wendland's laboratory in Berlin "at the sign of the Golden Angel in the street of the Moors" (*11*), (*40*).

In 1770 he became an assistant to the famous chemist, Valentin Rose, who, however, died only a few months later. Although Klaproth was only twenty-seven years old when this emergency arose, he met all the responsibilities of his new position. He not only carried on Rose's duties for nine years, but acted as a father to his two fatherless sons, providing carefully for their education. The younger boy unfortunately died in childhood, but the older one, Valentin Rose the Younger, shared Klaproth's love for nature, and collaborated with him in many researches. It was

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* "It is only the truth that we want to know, and isn't it a glorious feeling to have discovered it?"

Rose's task to repeat and verify all Klaproth's experiments before the results were published (*11*). Klaproth afterward purchased the Flemming laboratory on Spandau Street. His marriage to Sophie Christiana Lekman led to a happy family life. They had four children, and the only son, Heinrich Julius, became a famous Orientalist.

Martin Heinrich Klaproth made many brilliant contributions to analytical and mineralogical chemistry (*33*), and his papers are assembled in his "*Beiträge zur chemischen Kenntniss der Mineralkörper,*" a six-volume work. Although he never discovered an element in the sense of isolating it for the first time, his analytical work foreshadowed the discovery of uranium and zirconium and verified the discovery of tellurium and titanium.

In 1789 he investigated the mineral pitchblende, which was then thought to be an ore of zinc and iron. When he dissolved it in nitric acid, however, and neutralized the acid with potash, he obtained a yellow precipitate which dissolved in excess potash. Klaproth concluded correctly that the mineral must contain a new element, which he named in honor of the new planet, Uranus, which Herschel had recently discovered (*12*). He then attempted to obtain metallic uranium just as Hjelm had prepared metallic molybdenum. By strongly heating an oil paste of the yellow oxide in a charcoal crucible, he obtained a black powder with a metallic luster, and thought he had succeeded in isolating metallic uranium (*29*). For over fifty years the elementary nature of his product was accepted by chemists, but in 1841 Peligot showed that this supposed uranium metal was really an oxide.

MARTIN HEINRICH KLAPROTH
1743–1817

German chemist and pharmacist. The most distinguished German mineralogical and analytical chemist of his time. His careful analyses led to the discovery of uranium and zirconium and verified the discovery of tellurium and titanium. He also made pioneer researches on ceria.

When the University of Berlin was founded, Klaproth was sixty-seven years old, yet he was appointed as the first professor of chemistry, and served in that capacity until his death on January 1, 1817 (*13*). Thomas Thomson mentioned as his most characteristic personal traits: pure love of science, intellectual integrity, unselfishness, modesty, friendliness, kindness, a sense of humor, religious feeling, freedom from superstition, neatness, and precision (*14*).

In 1823 J. A. Arfwedson reduced the green oxide of uranium (then believed to be the lowest oxide) with hydrogen, and obtained a brown powder which he took to be the metal, but which is now known to be uranous oxide, UO_2 (*15*), (*30*). In 1841 Peligot, on analyzing anhydrous uranous chloride, UCl_4, found that 100 parts of this chloride apparently yielded about 110 parts of its elements uranium and chlorine. His explanation of this seemingly impossible result was that the uranous chloride reacts with water in the following manner:

$$UCl_4 + 2H_2O = UO_2 + 4HCl$$

Since uranous oxide cannot be reduced with hydrogen or carbon, it had always been mistaken for metallic uranium.

Peligot then heated the anhydrous chloride with potassium in a closed platinum crucible. This was heroic treatment for the platinum, to be sure, for the reaction was violent enough to make crucible and contents white-hot. However, since he took care to place the small crucible inside a larger one and to remove his alcohol lamp as soon as the reaction had started, Peligot avoided being injured by the pieces of potassium thrown out of the crucible. When the violent reaction subsided, he heated the crucible strongly to remove the excess potassium and to make the reduced uranium coherent. After cooling it, he dissolved out the potassium chloride, and obtained a black metallic powder with properties quite different from those

From Ferchl's "Von Libau bis Liebig"

THE ROSE PHARMACY IN BERLIN*

Valentin Rose the Elder (1735–1771), his son Valentin Rose the Younger (1762–1807), and his grandson Heinrich Rose (1795–1864) all rendered distinguished service to chemistry and pharmacy.

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* Reproduced by courtesy of Mr. Arthur Nemayer, Buchdruckerei und Verlag, Mittenwald, Bavaria.

formerly attributed to metallic uranium (*15*), (*31*). He was evidently the first person to isolate this metal.

Eugène-Melchior Peligot was born on February 24, 1811, at Paris. He studied at the Lycée Henri IV and at the Central School of Arts and Manufactures, but was obliged to leave school for financial reasons. In 1832, however, good fortune dawned for him, and he was admitted to the laboratory of the École Polytechnique to study under J. B. Dumas. A few years later he was collaborating with Dumas in important researches in organic chemistry.

For thirty-five consecutive years Peligot occupied the chairs of analytical chemistry and glass-making at the Central School of Arts and Manufactures, and during this time he wrote an important treatise on each of these subjects. He also lectured to large, sympathetic audiences at the Conservatoire des Arts et Métiers, and taught a course in agricultural chemical analysis at the National Agronomic Institute.

He was employed at the Mint for forty years, first as assayer, then as verifier, and finally as Director of Assays. His residence was at the Mint also, and it was there that he died in 1890. According to Tissandier, "his life, always calm and methodical, was entirely consecrated to the science that he loved with passion and to his family that he cherished no less" (*34*). He must have been a man of broad interests, for he published papers on such varied topics as: water analysis, the chemical composition of the sugar beet and sugar cane, chemical and physiological studies of silk-worms, the composition of Bohemian glass, and researches on uranium and chromium (*6*).

From Ferchl's "Von Libau bis Liebig'

VALENTIN ROSE THE YOUNGER
1762–1807*

German chemist and apothecary who was educated by Klaproth, collaborated with him in his researches and verified all his analyses before publication. Rose demonstrated the presence of chromium in a species of serpentine. He was the father of Heinrich Rose, the chemist, and Gustav Rose, the mineralogist. His father, Valentin Rose the Elder, was the discoverer of the low-melting alloy, Rose's metal.

Chromium

Nicolas-Louis Vauquelin, the discoverer of the metal chromium, was

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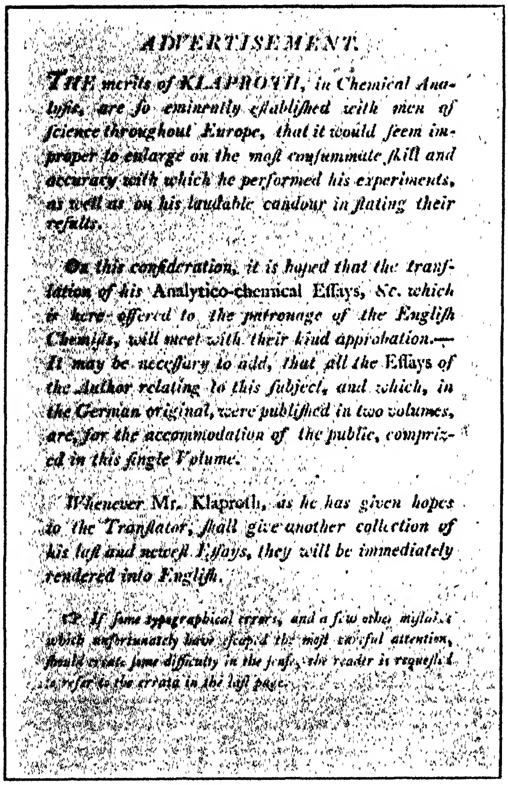
* **Reproduced by courtesy of Mr. Arthur Nemayer, Buchdruckerei und Verlag, Mittenwald, Bavaria.**

born on May 16, 1763, in a little Normandy village called St. André d'Hébertot.* As a child he worked in the fields with his father, who struggled hard to feed and clothe his large family. The boy made surprisingly rapid progress in the village school and in the religious studies taught him by the curé, who was very fond of him (*16*). At the age of fourteen years, young Vauquelin became a laboratory assistant and dishwasher in an apothecary shop in Rouen, and somewhat later he went to Paris with a letter of introduction from his old curé at St. André d'Hébertot to the prior of the order of Prémontré. His two best friends during his early struggles in Paris were this venerable prior and Mme. Aguesseau, the owner of the estate on which the elder Vauquelin worked as a peasant (*16*).

During his first three years in the city, the boy worked in various apothecary shops, and in his leisure moments studied Latin and botany. One of these pharmacies was owned by M. Cheradame, a cousin of the famous chemist, Antoine-François de Fourcroy. When M. Cheradame told Fourcroy about young Vauquelin's fondness for chemistry, Fourcroy immediately engaged the boy as his assistant and took him home. Fourcroy's unmarried sisters treated the young assistant with all gentleness and kindness, and on one occasion he owed his recovery from a serious illness to their motherly care, an act of kindness which he never forgot.



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THE merits of KLAPROTH, in Chemical Analyſis, are ſo eminently eſtabliſhed with men of ſcience throughout Europe, that it would ſeem improper to enlarge on the moſt conſummate ſkill and accuracy with which he performed his experiments, as well as on his laudable candour in ſtating their reſults.

On this conſideration, it is hoped that the tranſlation of his Analytico-chemical Eſſays, *&c. which is here offered to the patronage of the Engliſh Chemiſts, will meet with their kind approbation.—It may be neceſſary to add, that all the* Eſſays *of the Author relating to this ſubject, and which, in the German original, were publiſhed in two volumes, are, for the accommodation of the public, comprized in this ſingle Volume.*

Whenever Mr. Klaproth, *as he has given hopes to the Tranſlator, ſhall give another collection of his laſt and neweſt Eſſays, they will be immediately rendered into Engliſh.*

☞ *If ſome typographical errors, and a few other miſtakes which unfortunately have eſcaped the moſt careful attention, ſhould create ſome difficulty in the ſenſe, the reader is requeſted to refer to the errata in the laſt page.*

TRANSLATOR'S PREFACE TO THE ENGLISH EDITION OF KLAPROTH'S "ANALYTICAL ESSAYS TOWARD PROMOTING THE CHEMICAL KNOWLEDGE OF MINERAL SUBSTANCES"

Vauquelin continued his study of physics, chemistry, and philosophy, and assisted Fourcroy in teaching a course at the Athenaeum. He was diffident about speaking in public, but as soon as he became acquainted with his new

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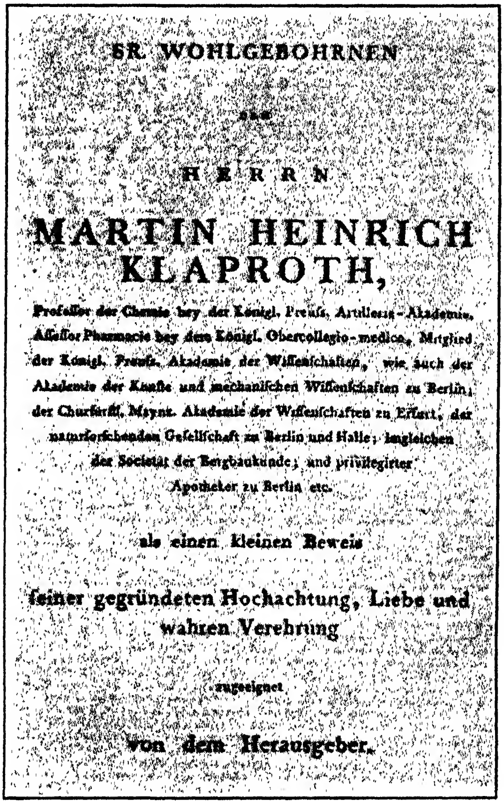
* Also spelled Saint-André des Berteaux.

students, he always taught with pleasure and enthusiasm and soon endeared himself to them.

One of the stirring events of the French Revolution was Vauquelin's rescue, from the mob, of an unfortunate Swiss soldier, who had escaped from the Tuileries massacre. Because of his participation in the Revolution, Vauquelin had to leave Paris in 1793; however, after serving as pharmacist in a military hospital for a few months, he returned to Paris to teach chemistry at the Central School of Public Works, which afterward became the École Polytechnique. He later became an inspector of mines and professor of assaying at the School of Mines, where he also lived. Out of gratitude to Fourcroy's sisters, who continued to keep house for him even after the death of their brother, Vauquelin placed most of the apartment at their disposal, and both the sisters lived with him until they died (*16*), (*35*).



SR. WOHLGEBOHRNEN

dem

HERRN

MARTIN HEINRICH
KLAPROTH,

Profeſſor der Chemie bey der Königl. Preuſs. Artillerie-Akademie,
Aſſeſſor Pharmacie bey dem Königl. Obercollegio-medico, Mitglied
der Königl. Preuſs. Akademie der Wiſſenſchaften, wie auch der
Akademie der Künſte und mechaniſchen Wiſſenſchaften zu Berlin,
der Churfürſtl. Maynz. Akademie der Wiſſenſchaften zu Erfurt, der
naturforſchenden Geſellſchaft zu Berlin und Halle; ingleichen
der Societät der Bergbaukunde; und privilegirter
Apotheker zu Berlin etc.

als einen kleinen Beweis

ſeiner gegründeten Hochachtung, Liebe und
wahren Verehrung

zugeeignet

von dem Herausgeber.

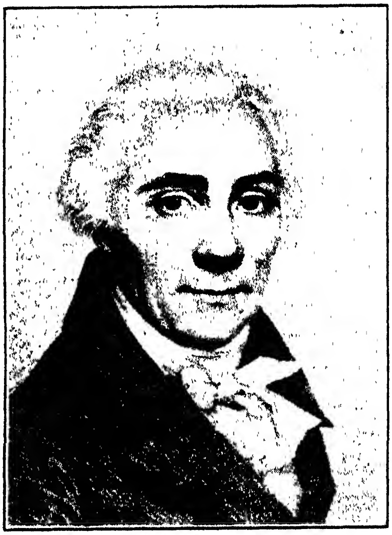
DEDICATION OF THE GERMAN EDITION OF SCHEELE'S WORKS EDITED BY HERMBSTÄDT

The first analysis of the Siberian red lead (now known as crocoite, or crocoisite) was made by Johann Gottlob Lehmann in 1766 (*43*). He was highly esteemed as director of the Prussian mines and as a lecturer in Berlin. In 1761 he became professor of chemistry and director of the Royal Museum in St. Petersburg, and was commissioned by Catherine II to make extensive mineralogical trips throughout the Russian Empire. He described the Siberian red lead in a letter to the Comte de Buffon in 1766. At that time it was found only at a smelter fifteen versts from Ekaterinstadt (Markstadt). In his chemical investigation of it, Lehmann dissolved it in hydrochloric acid, noticed the emerald-green color of its (reduced) solution, and found that the mineral contained lead. He concluded that it must be "a lead mineralized with a selenitic spar and iron particles" (*44*). In 1767 his life was suddenly cut short by the bursting of a retort in which he was heating some arsenic (*45*).

In 1770 P. S. Pallas described the Beresof gold mines near Ekaterinburg, Siberia. On the 25th and 26th of June of that year he wrote: "The Beresof pits include four mines, which have been worked since 1752." The Beresof mine also yielded copper, lead, and silver. "A very remarkable red lead mineral is also exploited there," said Pallas, "which has never been found in any other mine of the Empire or elsewhere. This lead ore is heavy, of varying color (sometimes like that of cinnabar), and semi-transparent . . . . One also finds small irregular, tortuous pyramids of it attached like little rubies to quartz. When pulverized, it gives a handsome yellow guhr which could be used in miniature painting . . . . It is difficult today to procure enough of it for large-scale assays, for the part of the mine where this lead ore is found is seldom worked, for lack of air . . . . Five hundred workmen are now employed in these mines . . ." (*46*).

EUGÈNE PELIGOT
1811–1890

Professor of analytical chemistry and glass-making at the Central School of Arts and Manufactures in Paris. Director of assays at the Paris Mint. Professor of agricultural chemical analysis at the National Agronomic Institute. The first to isolate the metal uranium.



NICOLAS-LOUIS VAUQUELIN
1763–1829

French analytical and mineralogical chemist and apothecary of the Revolutionary Period. Professor at the École Polytechnique and at the School of Mines. Assayer at the Paris Mint. In 1797 he discovered chromium and beryllium.

Peter Simon Pallas (1741–1811) was a native of Berlin. He was broadly educated in medicine, natural sciences, and modern languages, which he studied in Berlin, Halle, Göttingen, the Netherlands, and England. From 1768 until 1774 he made extended journeys at the request of Catherine II and suffered great privations in order to study the natural history of Siberia, the Altai Mountains, the lower Volga region, and the southern part of European Russia (*47*), (*48*), (*49*).

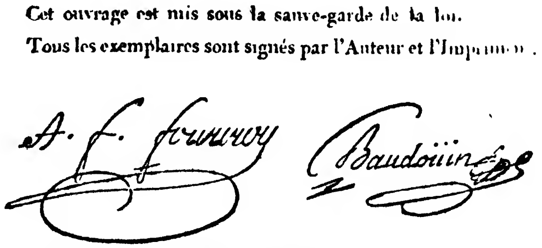
In 1798 N.-L. Vauquelin analyzed crocoite and gave a detailed account of its history. "All the specimens of this substance which are to be found in the several mineralogical cabinets in Europe," said he, "were obtained from this [Beresof] gold mine; which indicates that it was formerly abundant; but it is said that for some years past it has become very scarce, and that at present it is bought for its weight in gold, especially if pure and regularly formed. The specimens which do not possess the regular figure, or are broken into fragments, are appropriated to painting, in which art this substance is of high value for its beautiful orange-yellow colour, its unchangeableness in the air, and the facility with which it can be levigated with oil" (*36*).

The Naturalist's Library, vol. 9

PETER SIMON PALLAS
1741–1811

German scientist who made extensive scientific journeys to study the natural history of Russia and Siberia. He described the Beresof gold mines and the "Siberian red lead" (crocoite) in 1770.

"The beautiful red colour, transparency, and crystalline figure of the Siberian red lead," continued Vauquelin, "soon induced mineralogists and chemists to make enquiries into its nature. The place of its discovery, its specific gravity, and the lead ore which accompanies it produced an immediate suspicion of the presence of that metal; but, as lead had never been found in possession of the characteristic properties of this Siberian ore, they thought, with justice, that it was mineralised by some other substance; and Lehmann, who first subjected it to chemical analysis, asserted, in a Latin dissertation printed at Petersburgh in 1766 . . . that the mineralisers were arsenic and sulphur" (*36*). When Vauquelin and Macquart analyzed it, they found it to consist of lead peroxide, iron, and aluminum. Bindheim of Moscow reported, however, that it contained molybdic acid, nickel, cobalt, iron, and copper. To settle this question Vauquelin in 1797 repeated the analysis (*32*). When he boiled the pulverized mineral with two parts of potassium carbonate, he obtained lead carbonate and a yellow solution containing the potassium salt of an unknown acid. This solution gave a beautiful red precipitate when added to the solution of a mercuric salt and a yellow precipitate when added to a lead solution. He noticed also that when he isolated the new acid and added stannous chloride, the solution became green (reduction of chromic acid to a chromic salt) (*17*).


Cet ouvrage est mis sous la sauve-garde de la loi.
Tous les exemplaires sont signés par l'Auteur et l'Imprimeur.

A. F. Fourcroy Baudouin

FOURCROY AUTOGRAPH FROM HIS *"Système des Connaissances Chimiques"*

In the following year Vauquelin succeeded in isolating the new metal. After removing the lead in the Siberian red lead by precipitation with hydrochloric acid, he evaporated the filtrate to obtain the chromium trioxide, which he put into a charcoal crucible placed inside a large earthen one filled with charcoal dust. After heating it intensely for half an hour, he allowed it to cool. The inner crucible was found to be filled with a network of gray, interlacing metallic needles which weighed one-third as much as the original chromium trioxide that had been reduced. Because of its many colored compounds Fourcroy and Haüy suggested the name *chromium* for the new metal (*17*), (*36*).


ANTOINE-FRANÇOIS DE FOURCROY
1755–1809

French chemist of the Revolutionary Period. Defender of Lavoisier's views on combustion. In collaboration with Lavoisier, de Morveau, and Berthollet he carried out a reform of chemical nomenclature. Fourcroy prepared and analyzed many reagents and medicinals.

Vauquelin taught for a time at the Collège de France and at the Jardin des Plantes, and in 1811, upon the death of his old friend and teacher, M. Fourcroy, he became his successor as professor of chemistry in the School of Medicine. In 1828 the Department of Calvados, in which his native village of St. André d'Hébertot is situated, appointed him as one of its deputies. He discharged the duties of this office with honor, striving always for the best interests of his beloved Republic. Although his early days were spent in poverty and toil, he became a man of broad culture, took pleasure in music and literature, and frequently quoted his favorite authors, Horace and Virgil (*16*).

M. Chevallier, one of his students, recalled an incident that well illustrates Professor Vauquelin's kindness. In 1808 Bonaparte ordered the arrest and deportation of all Spaniards living in Paris. One of the sixty who were seized and taken to the prefecture of police was a young man who had recently come to study under Professor Vauquelin and who had no other protector in Paris. Vauquelin started out before six o'clock next morning, dressed in the uniform worn on formal occasions by members of the Institute, went to the police station, and succeeded in having the boy released. This young Spaniard, who was named Orfila, afterward made a name for himself in chemistry (*16*), (*35*).

MATHIEU-JOSEPH-BONAVENTURE ORFILA
1787–1853

Spanish chemist who studied under Vauquelin in Paris. The founder of modern toxicology. Professor of toxicology, medical chemistry, and forensic chemistry in Paris.

Sir Humphry Davy once gave the following amusing description of Vauquelin's home life:

> Vauquelin was in the decline of life when I first saw him in 1813—a man who gave me the idea of the French chemists of another age; belonging rather to the pharmaceutical laboratory than to the philosophical one; yet he lived in the Jardin du Roi. Nothing could be more singular than his manners, his life, and his ménage. Two old maiden ladies, the Mademoiselles de Fourcroy, sisters of the professor of that name, kept his house. I remember the first time that I entered it, I was ushered into a sort of bed-chamber, which likewise served as a drawing-room. One of the ladies was in bed, but employed in preparations for the kitchen; and was actually paring truffles. Vauquelin wished some immediately to be dressed for my breakfast, and I had some difficulty to prevent it. . . . (*18*).

This was, to be sure, an unusual way of receiving a fashionable English gentleman, but perhaps if Sir Humphry had known the pleasing story of Vauquelin's gratitude to the two old ladies who had befriended him in youth, he would not have been so critical.

Vauquelin in France and Klaproth in Germany were the outstanding analytical chemists of their day, and were, in fact, two of the greatest analysts of all time. According to Thomson, Vauquelin was "by far the most industrious of all French chemists" (*19*). He died in his native district at the Château des Berteaux on November 14, 1829.

Chromium has taken its place among the world's useful metals, and stainless steel, chromium-plated hardware and automobile trimmings, and artistic chromium jewelry now bear witness to the importance of Vauquelin's discovery.

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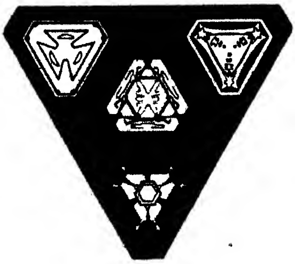

VIII. THE SCIENTIFIC CONTRIBUTIONS OF THE DE ELHUYAR BROTHERS*

Although Don Fausto de Elhuyar† and his brother, Don Juan José, achieved undying fame by their isolation of the element now known as tungsten, only meager accounts of their contributions have been recorded in the English language, and even in Spanish and Spanish-American journals it is difficult to find more than brief mention of Don Juan José. This Castilian literature, however, contains a wealth of information about the scientific activities of Don Fausto, and the observance of the centenary of his death brought forth new biographical material.

. . . .

In the latter part of the eighteenth century the Count of Peñaflorida, with the approval of King Charles III, founded in the Basque provinces a patriotic organization known as "The Basque Society of Friends of their Country" (*Sociedad Vascongada de Amigos del País*). In the early days of its existence, this learned society, consisting of studious men of the nobility and clergy, used to meet every evening in the week. On Mondays they discussed mathematics; on Tuesdays they made experiments with Abbé Nollet's electrical machine or with their air pump from London or discussed the physical theories of the day, such as Franklin's views on electricity; on Wednesdays they read history and translations by members of the society; on Thursdays they listened to music; on Fridays they studied geography; on Saturdays they conversed on current events; and on Sundays they again listened to music. According to a contemporary writer, Don Juan Sempere y Guarinos (*1*):

> The two most glorious monuments of the *Sociedad Vascongada* are the Seminary of Vergara and the House of Mercy of Vitoria...This Seminary was the first in Spain in which virtue was united with the teaching of the sciences most useful to the state. Vergara was the first town in which chairs of chemistry and metallurgy were founded.

Soon after this Seminary was founded in 1777, two brilliant and promising youths of Basque and French lineage, Don Juan José de Elhuyar y de Zubice and his younger brother, Don Fausto, were commissioned to study abroad. Don Juan José was sent by the King to master the science of metallurgy and Don Fausto was chosen by the Count of Peñaflorida to study mineralogy at the expense of the Society of Friends of their Country and become the first professor of that subject at the new Seminary (*2*).

Don Fausto was born at Logroño in northern Spain on October 11, 1755, and was educated in Paris under the best masters. While the gifted young

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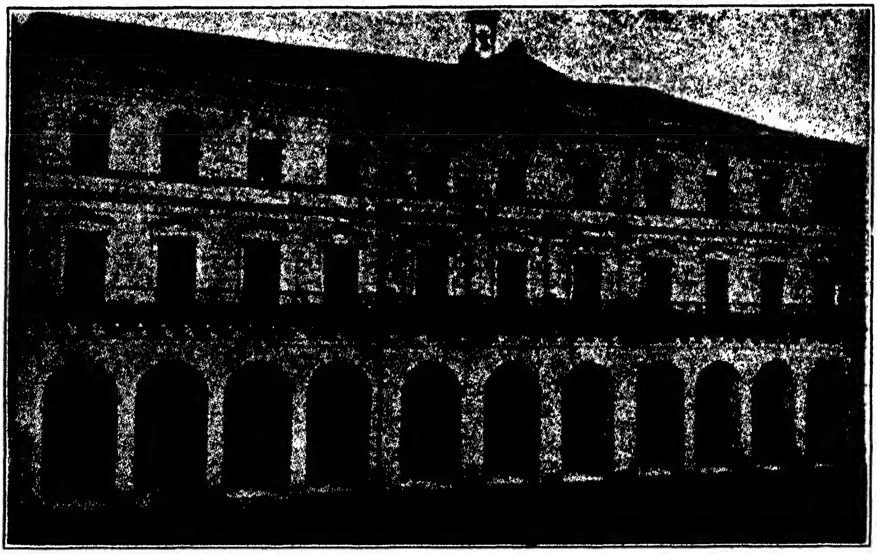
* Presented before the Division of History of Chemistry at the Chicago meeting of the A. C. S., Sept. 11, 1933.

† Even in Spanish literature, the spelling of this name varies.

Louis-Joseph Proust (*3*), who later defended the law of definite proportions so valiantly against Berthollet, taught chemistry at Vergara, Don Fausto and Don Juan José went to Freiberg, where in 1778 they enrolled as students in the Royal School of Mines, studied subterranean geometry, mining, metallurgy, and machine construction, and became ardent disciples of the great mineralogist Abraham Gottlob Werner. They also visited the mines and metallurgical industries of Sweden and England, and at least one of the brothers profited by a brief course of study at Upsala under the celebrated Torbern Bergman.



Courtesy Dr Moles and Mr. de Gálvez-Cañero

THE SEMINARY OF VERGARA

It was here that Don Juan José and Don Fausto de Elhuyar carried out their remarkable analysis of wolframite, which resulted in the isolation of a new metal, "wolfram," or tungsten. Among the professors at this Seminary were L.-J. Proust, François Chabaneau, and Fausto de Elhuyar.

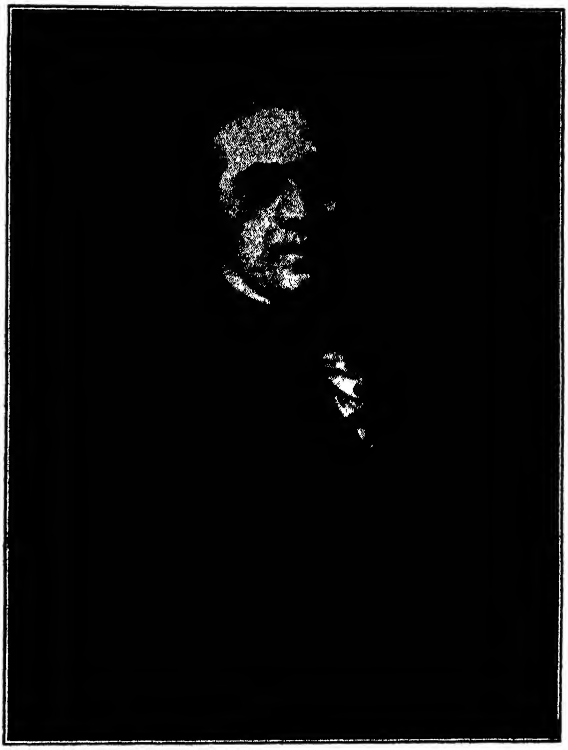
When Don Fausto took up his teaching duties at Vergara just after the Christmas vacation in 1781,* he was already famous because of his achievements in northern Europe. He soon published papers on the manufacture of tin plate, the mines of Somorrostro, the iron-works of Biscaya, and the working of copper mines.

Soon after devoting themselves to laboratory research in Vergara, the de Elhuyar brothers analyzed a specimen of wolframite from a tin mine in Zinnwald and separated from it an insoluble yellow powder which they

* The author wishes to correct a statement in Reference 8. Elhuyar taught at Vergara *before* going to Mexico, not after his return.

called wolframic acid and which they later showed to be identical with tungstic acid. Since these Spanish chemists were the first to reduce wolframic acid, Dr. E. Moles of the University of Madrid and the late Dr. Fages y Virgili have pointed out that the metal ought to be called by the name *wolframium* (*wolfram*) which the de Elhuyar brothers gave it. Although this name (*4*) has been changed in some languages to forms derived from *tungstein*, the accepted international symbol, *W*, still bears witness that the metal was first obtained from wolframite, not from *tungstein* (scheelite).

Although the isolation of this metal has sometimes been erroneously credited to Don Fausto alone, the original paper published in 1783 in the *Extractos de las Juntas Generales* of the Royal Basque Society under the title "Chemical Analysis of Wolfram and Examination of a new Metal which Enters into its Composition" bore the names of both brothers. Because of the great importance of this memoir it was soon translated into French, English, and German (*5*).



Courtesy Dr. Moles and Mr. de Gálvez-Cañero

FAUSTO DE ELHUYAR, 1755–1833, AS HE APPEARED WHILE STUDYING IN VIENNA BEFORE GOING TO MEXICO

At this period he was already famous because of the research at Vergara in which he and his brother liberated the element now known as tungsten. This portrait was bequeathed to the Mining Council by Don Fausto's daughter, Doña Luisa de Elhuyar de Martinez de Aragón.

Dr. Fages and Dr. Moles have both pointed out that, in isolating the new metal, the de Elhuyar brothers did much more than merely confirm the hypothesis of Bergman. Instead of analyzing tungstic acid intentionally prepared to test this hypothesis, as has so often been stated, they analyzed *wolfram* without any preconceived ideas. Dr. Fages stated that, after the de Elhuyar brothers had discovered the acid in wolframite:

. . .their great enlightenment and erudition, supporting their great genius, caused them to suppose that the earth encountered, completely new to them and to almost all chemists, might be the same that Scheele had discovered a few months before in another mineral, entirely independently. . .(*4*), (*6*).

From F. G. Corning, "A Student Reverie"

ABRAHAM GOTTLOB WERNER, 1750–1817

Professor of geognosy at the Freiberg School of Mines. Because his followers believed in the aqueous origin of rocks, they were called Neptunists. Among his distinguished students were the de Elhuyar brothers, Baron Alexander von Humboldt, and A. M. del Río, the discoverer of vanadium (erythronium).

The de Elhuyar brothers concluded from their analysis that wolframite is composed of wolframic acid combined with iron and manganese. Their method of obtaining the metal by reduction of tungstic (wolframic) acid with charcoal has been described in other papers (*4*), (*6*), (*7*), (*8*). As late as 1786 the great analytical chemist, Martin Heinrich Klaproth, admitted that all his own attempts had failed and that "up to the present only Hr. Elhuyar has succeeded in getting the metal" (*9*).

Although the de Elhuyar brothers were unsuccessful in their attempts to synthesize wolframite, they foreshadowed modern methods of mineral synthesis (*3*). They also devised an ingenious method of determining the specific gravity of solids, and their values for wolframite, tungsten trioxide, and metallic tungsten were surprisingly accurate (*2*). Their dissertation on wolframite, published three-quarters of a century before Thomas Graham founded the science of colloid chemistry, contains a clear description of a wolframic (tungstic) acid sol (*2*). Spanish writers have commented on the lucid and refined style of this great memoir, which, though written in the phraseology of the phlogistonists, exhibits scientific concepts and technic which are astonishingly modern. In the French translation of it, the de Elhuyar brothers modestly admit that no use has yet been found for the new metal, but add that "we must not conclude from this that it is entirely useless" (*3*).

In the meantime, events in the western hemisphere had caused King Charles to make new plans for the de Elhuyar brothers. As early as 1774 Don Joaquín de Velázquez Cárdenas y León had presented a plan for the establishment of a school of mines at Mexico City which had received the King's approval. However, the realization of the plan had unfortunately been deferred by the death in 1786 of this distinguished Mexican scientist. In order to fulfill his cherished hope of developing the mines of America, King Charles sent Don Juan José to New Granada (Colombia) and Don Fausto to Hungary and Germany to prepare himself for the exacting duties of Director General of Mines of Mexico (*2*), (*6*).

DON ANDRÉS MANUEL DEL RÍO,* 1764–1849

Professor of mineralogy, French, and Spanish at the School of Mines of Mexico. Member of the American Philosophical Society. He discovered the element vanadium (erythronium), but later confused it with chromium. This portrait belongs to the School of Mines of Mexico.

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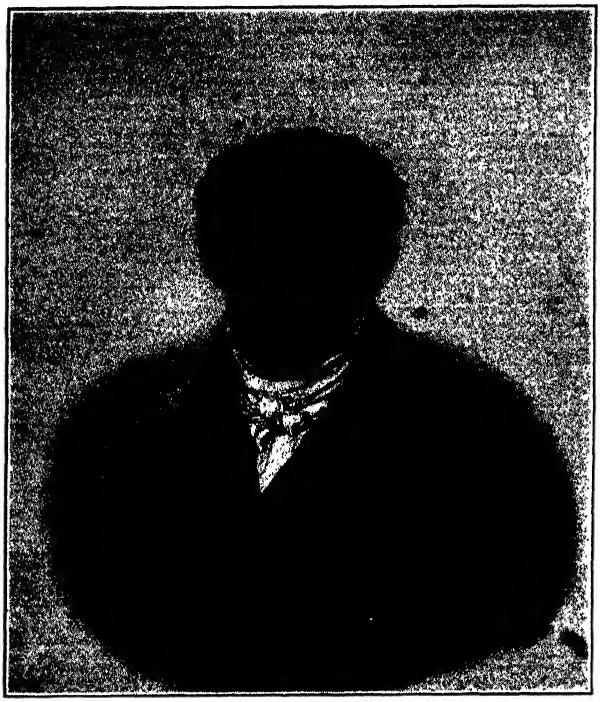
* The author wishes to thank Señor Pablo Martínez del Río, head of the Extension Dept. of the National University of Mexico, for his kind assistance in locating this portrait.



Courtesy F. B. Dains

BARON ALEXANDER VON HUMBOLDT, 1769–1859

German naturalist and traveler. Author of "Kosmos" and "Political Essay on New Spain." Friend of Fausto de Elhuyar and A. M. del Río.

The former served for many years as professor of mineralogy, successfully administered technical commissions of great responsibility, and developed the mines of New Granada. Early in the spring of 1786 Don Fausto collaborated with François Chabaneau, professor of chemistry at Vergara, in some remarkable researches on platinum. In a letter written in Vergara on March 17th of that year to Don Juan José, who was then living in Bogotá, Colombia, Don Fausto gave a clear description of their process for making pure platinum malleable. In his bibliography of Spanish science, Menéndez y Pelayo mentions a paper on locating veins of mercury which Don Juan José published in the same year (*10*).

Don Juan José was a highly esteemed friend of the great Spanish botanist, Don José Celestino Mutis, who once said proudly, "I have been the instrument for the glorious acquiring of the two learned D'Elhuyar [*sic*] brothers and the rapid introduction of Baron Born's new mining process" (*11*). In 1932 the Republic of Colombia celebrated the bicentenary of the birth of this great Spanish botanist (*12*). According to Dr. Fages, many documents preserved with the famous Mutis collection at the Botanical Garden in Madrid show that the services of Don Juan José in New Granada were no less useful to Spain than those of his younger brother in Mexico. Don Juan José de Elhuyar died in 1804 in the Santa Ana mine at Bogotá, without ever revisiting his native land (*6*), (*11*).

On May 22, 1783, while the de Elhuyar brothers were still engrossed in their famous experiments on wolframite, the King had issued his "Royal Ordinances for the Direction, Management, and Government of the

Important Body of Mining in New Spain and of its Royal General Tribunal (*13*)." In the spring of 1786 Don Fausto de Elhuyar was sent to Hungary and Germany to study the new method of amalgamation which Counselor Born had established in Schemnitz and Freiberg. On July 18th of that year the Marquis of Sonora wrote as follows to Don Fausto, who was then in Vienna:

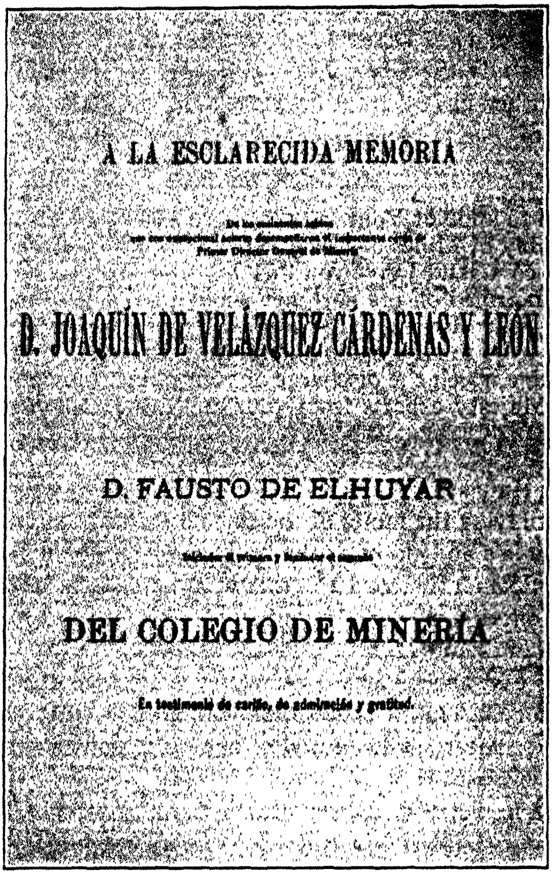
> The King has deigned to appoint Your Excellency as Director General of the Royal Assembly of Mines of Mexico with a salary of 4000 pesos, and by his Royal command I give you this order for your satisfaction, and that, well informed on the new method of amalgamation that Mr. Born invented, you may return to those realms at your earliest convenience in order to go to New Spain and fill that office with the intelligence and knowledge which the discharge of your obligation demands and which His Majesty expects from your application, proficiency, and zeal (*13*).

After a year and a half in Hungary and Germany, Professor Elhuyar spent a few months in Vienna studying the mines of the surrounding region and the metallurgy of many metals and enjoying the brilliant social life of the city. Before returning to Spain he married a German lady of distinguished lineage, Juana Raab de Moncelos, who, in the middle of June, 1788, set sail with him from Cadiz for New Spain (*11*), (*21*).

When the frigate *Venus* cast anchor at Vera Cruz on September 4th of that year, the new Director General of Mines disembarked and went immediately to Mexico City. After a solemn and colorful ceremony in the Royal Palace, he entered at once into his new duties.

A few months later, as a first step in the construction of a chemical laboratory, assay furnaces were built in the patio of the college building. According to Director Elhuyar's plan, the students admitted were to range in age from fifteen to twenty years and were to wear a prescribed blue uniform with red collar and cuffs and gold buttons decorated with the signs for gold, silver, and mercury. On Sundays and church holidays they were expected to attend the church functions, both morning and afternoon, and to call on the mining officials "in order to learn the usages of polite society (*13*)." As an incentive to scholarship, the Director arranged that prizes for good conduct and industry should be awarded with great solemnity. These consisted of ornaments to be worn in the buttonhole (*13*). The School of Mines was officially opened on New Year's Day, 1792, with an impressive ceremony in the Church of San Nicolás. It was the first scientific institution to be erected on Mexican soil (*14*).

The new Director of Mines made a thorough experimental study of the "patio," or cold amalgamation, process of separating silver from its ores. Although this empirical process invented by Bartolomé de Medina had been used for more than two centuries, no satisfactory explanation of the



A LA ESCLARECIDA MEMORIA

D. JOAQUÍN DE VELÁZQUEZ CÁRDENAS Y LEÓN

D. FAUSTO DE ELHUYAR

DEL COLEGIO DE MINERÍA

En testimonio de cariño, de admiración y gratitud.

DEDICATION OF THE HISTORY OF THE COLLEGE OF MINES OF MEXICO (Ref. *13*)

Translation: "To the illustrious memory of the eminent scientists who filled with exceptional ability the important office of First Director General of Mining, D. Joaquín de Velázquez Cárdenas y León and D. Fausto de Elhuyar, the former the initiator and the latter the founder of the College of Mines. In testimony of affection, admiration, and gratitude."

chemical reactions involved had yet been given. L.-J. Proust, who was then teaching in the Academy of Artillery at Segovia, reviewed these remarkable experiments of Elhuyar in volume one of the *Anales del Real Laboratorio de Química* in 1791. The late Señor J. R. Mourelo once stated that ". . . the glory of both [Bartolomé de Medina and Alvaro Alonso Barba] shines and scintillates more brightly in that of . . . the famous mining engineer, Don Fausto Elhuyar, in whom appears completed . . . the magnificent work of those eminent miners . . ." (*15*).

Since a royal order, transmitted through the Viceroy of Mexico, had decreed that Werner's theory of the formation of veins be taught to the students, the brilliant young Don Andrés Manuel del Río was sent to Mexico to introduce the most approved mining methods which he had learned at Freiberg (*13*). Although del Río had declined the professorship of chemistry, he accepted that of mineralogy, and took with him on the warship San Pedro Alcántara a quantity of equipment for the School of Mines. Soon after his arrival in Mexico City in December, 1794, Don Fausto de Elhuyar asked him to translate Werner's book on the theory of formation of veins into Spanish (*13*).

Courtesy Dr. Moles and Mr. de Gálvez-Cañero

FAUSTO DE ELHUYAR, DIRECTOR GENERAL OF MINES OF SPAIN

The centenary of his death was observed in 1933 at the School of Mining Engineering of Madrid.

When Señor Elhuyar's nine-year term as Director was about to expire in 1797, his colleagues and students requested that he be reappointed for another nine years, or for life, or for whatever period might meet with Royal favor (*13*). The report stated that ". . . this Royal Seminary is persuaded that in this kingdom there is no other subject of the merit and circumstances so suited to this institution. . . as Sr. D. Fausto Eluyar [*sic*]." The officers of the school felt that no one else "would recognize the character and genius of the [Mexican] people." The association of mining engineers from all parts of Mexico also voted unanimously for his reappointment, and the request was granted (*13*).

In the meantime Don Fausto made many inspection trips to mining centers, supervised the installation of pumps of his own invention, and for several months taught the chemistry course, because of the illness of Don Luis Lindner. Under his leadership the prestige of the school increased, and students came from distant parts of Mexico to obtain a broad cultural foundation as well as a practical knowledge of mining. In April, 1798, the King ordered that some of the most promising youths be selected by examination to become directors and mining engineers in the viceroyships of Peru and Buenos Aires and the provinces of Quito, Guatemala, and Chile, and to establish safe, economical methods for the exploitation of the precious metals (*13*).

After Baron Alexander von Humboldt had visited Mexico in 1803, he wrote that "no city of the new continent, without excepting those of the

United States, presents scientific establishments so large and substantial as the Capitol of Mexico. I shall mention . . . the School of Mines, directed by the learned Elhuyar . . ." (*16*).

The Baron also stated that

> . . . a European traveler would be surprised to meet in the interior of the country, near the California boundary, young Mexicans reasoning on the decomposition of water in the operation of amalgamation in the open air. The School of Mines has a chemical laboratory, a geological collection classified according to Werner's system, and a physical laboratory, in which are to be found not only valuable instruments of Ramsden, Adams, Lenoir, and Luis Berthoud, but also models made in the same capitol with the greatest precision and of the best wood in the country. The best mineralogical work which Spanish literature possesses, the manual of mineralogy arranged by Señor del Río according to the principles of the Freiberg School, where the author studied, has been printed in Mexico (*16*).

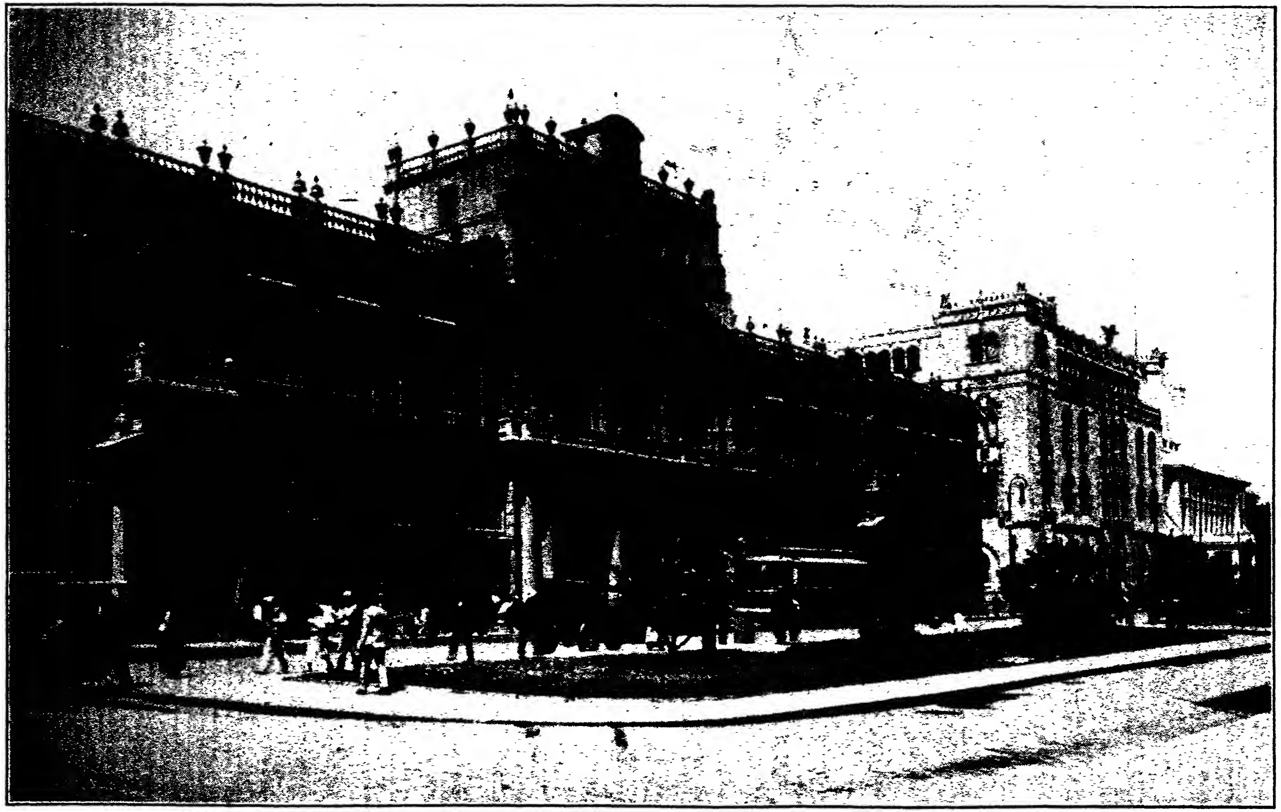
The Baron also mentioned Lavoisier's "Elements of Chemistry," the first Spanish edition of which was published in Mexico. Chaptal's textbook of chemistry was also used at the Mining Academy, but in 1820 it was superseded by that of Orfila (*13*).

Professor Elhuyar often ordered instruments for the School of Mines through von Humboldt, who selected and purchased them without any commission. In return for this courtesy he gave the Baron much valuable information for his "Political Essay on New Spain" (*13*), (*16*). Von Humboldt later presented to European museums numerous specimens of Mexican minerals which this Spanish scientist had given him.

Two of de Elhuyar's most famous papers were entitled "Suggestions on Coining in New Spain" and "Memoir on the Influence of Mining on the Agriculture, Industry, Population, and Civilization of New Spain" (*17*), (*18*). In his "History of Mexico" (*19*), H. H. Bancroft extolled the former treatise as follows:

> With regard to the mint and coinage I find the work of Fausto de Elhuyar, entitled Indigaciones sobre la Amonedación en la Nueva España, Madrid, 1818, to be extremely useful. His researches were conducted with great care, and supply a concise and correct history of the mint from its establishment down to the 10th of August, 1814, when he laid before the mining tribunal of Mexico, of which he was director, the results of his labors. In this book, which consists of 142 pages, he gives an account of the different coins struck off and the modifications which they experienced at different periods, also of the new system when the administration was assumed by the government. He moreover considers with attention the causes by which the interests of the mining industry suffered, and suggests remedies.

During the war of independence, the once prosperous mining industry of Mexico passed through such a serious depression that all courses at the



The School of Mines in Mexico City

School of Mines were suspended, with humane provision, however, for those of its employees who had no other source of income. Don Fausto de Elhuyar relinquished his authority, and thus, after thirty-three years of service, his directorship came to a close on October 22, 1821. The history of the School of Mines (*13*) by the distinguished mining engineer, Santiago Ramírez, contains a wealth of information about Elhuyar's services to Mexico.

After returning to Madrid, Professor Elhuyar was made a member of the General Council of Public Credit (*13*), served on many government commissions, wrote his famous treatise on the influence of mining in New Spain (*17*), drew up the new mining law known as the Royal Decree of July 4, 1825, and was made Director General of Mining* (*20*), (*22*). He planned the School of Mining Engineering of Madrid and organized and developed the mining industry of his native land, which he served devotedly to the end of his life. One of the reforms which he advocated was the eight-hour day (*2*).

In spite of his many positions of influence and responsibility, Professor Elhuyar lived in modest circumstances, devoting all his energy to intellectual rather than material pursuits. He died at Madrid on January 6, 1833, at the age of seventy-seven years. (Although the centenary of Elhuyar's death was observed on *February* 6, 1933, the death certificate which Señor de Gálvez-Cañero discovered in the records of San Sebastián parish in Madrid states that Don Fausto died on *January* 6th as the result of a fall (*11*).)

In 1892 the Mexican government under Porfirio Díaz, the former students of the Mining Academy, and the leading mining companies arranged a mining exposition and a series of public functions throughout the year to commemorate the centennial anniversary of the founding of the Seminary. All the scientific organizations in the country participated, and the German musical society, the *Orfeón Alemán*, gladly coöperated out of gratitude for the honors which the Seminary had bestowed on Baron von Humboldt. In each arch of the magnificent college building appeared a flag-draped escutcheon bearing an honored name, and foremost among these were Joaquín de Velázquez Cárdenas y León, Fausto de Elhuyar, and Andrés Manuel del Río (*14*).

On February 6, 1933, the Spanish Society of Physics and Chemistry, the Geological and Mining Institute of Spain, and the Association of Mining Engineers met at the School of Mining Engineering of Madrid to observe the one-hundredth anniversary of the death of Don Fausto de Elhuyar. Eloquent and scholarly addresses on the various phases of his services to

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* Although standard Spanish and German encyclopedias state that Don Fausto de Elhuyar also became Secretary of State, Dr. Fages (*6*) has pointed out that this is incorrect.

science were delivered by Señores Bermejo, Hauser, Gálvez-Cañero, Moles, Novo, and López Sánchez Avecilla, and three portraits* of him were displayed by Señor de Gálvez-Cañero, who published in 1933 a beautifully illustrated biography based on authentic documents and correspondence. Plans were announced for the publication of some of Don Fausto's papers in a series of Spanish scientific classics, and the Elhuyar Prize of 1000 pesetas was awarded to Don Fernando González Núñez for his revision of the atomic weight of chromium (*2*).

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The writer is deeply grateful to Professor E. Moles, Mr. Gálvez-Cañero, Dr. F. G. Corning, Señor Pablo Martínez del Río, and Dr. F. B. Dains for the use of the illustrations accompanying this chapter. It is also a pleasure to acknowledge the valuable help obtained from the literature on the history of Spanish chemistry which Dr. Moles and Mr. de Gálvez-Cañero so kindly contributed.

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* Señor Bermejo, president of the Spanish Society of Physics and Chemistry, also mentioned that there is a statue of Fausto de Elhuyar at the Faculty of Sciences of Saragossa.

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IX. TELLURIUM AND SELENIUM

It has been shown in preceding chapters that a number of elements including zinc, cobalt, nickel, manganese, hydrogen, nitrogen, oxygen, tungsten, molybdenum, and chromium were recognized and isolated during the eighteenth century. The story of tellurium, its discovery by Baron Müller von Reichenstein, and its confirmation by Klaproth remains to be told. Although selenium properly belongs in the early part of the nineteenth century, it is so closely related to tellurium both chemically and historically that it seems best to introduce it at this point. The scientific contributions and correspondence of Klaproth and of Berzelius furnish detailed information about these two great discoveries, and the "Early Recollections of a Chemist" by Friedrich Wöhler present an unforgettable picture of the great Swedish master.

. . . . . .

> *"The chymists are a strange class of mortals impelled by an almost insane impulse to seek their pleasure among smoke and vapour, soot and flame, poisons and poverty; yet among all these evils I seem to live so sweetly, that may I die if I would change places with the Persian King."* (*1*)

Tellurium*

The discoverer of tellurium, Franz Joseph Müller, was born on July 1, 1740, in Nagyszeben (Sibiu, or Hermannstadt) in the Transylvanian Alps (*14*). After studying law and philosophy in Vienna, he attended the School of Mines at Schemnitz (Selmeczbánya, or Štiavnica Banská), where he became intensely interested in mining, mineralogy, chemistry, and mechanics. At the age of twenty-eight years he became a surveyor in Hungary, and two years later he served so efficiently on a committee which managed the mines and smelters in the Banat that he was appointed surveyor and director of the mines. In 1775 he went to the Tyrol as mine captain and acting superintendent, and under Joseph II he became chief inspector of all the mines, smelters, and salt-works in Transylvania (*2*).

In 1782 Müller extracted from a bluish-white ore of gold (called *aurum problematicum, aurum paradoxum*, or *aurum album*), a metal which A. von Rupprecht thought to be antimony. Müller's paper announcing the discovery was entitled, "An Experiment with the Regulus Thought to Be Metallic Antimony Occurring in the Mariahilf Mine on Mt. Fazebay near Salatna."† Upon careful examination of the regulus, he decided in 1783 that although it bore some resemblance to antimony, it must be a new metal, different from all others. Seeking confirmation of his discovery,

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* See also Chapter X, pp. 169–82.

† *"Versuch mit dem in der Grube Mariahilf in dem Gebirge Fazebay bei Salatna vorkommenden vermeinten gediegenen Spiessglaskönig."*

Berzelius

From "Jac. Berzelius, Selbstbiographische Aufzeichnungen," Kahlbaum Monographs, Heft 7

YOUTHFUL PORTRAIT OF BERZELIUS

Left an orphan early in life, he was educated by his stepfather. Berzelius studied at the Linköping Gymnasium and later at the University of Upsala, where he received the degree of Doctor of Medicine. He was a student of Ekeberg, the discoverer of tantalum.

he sent a tiny specimen to Bergman; but, with such a small sample, the latter could do no more than prove that it was not antimony (*3*), (*11*).

Müller's important discovery seems to have been overlooked for fifteen years, but on January 25, 1798, Klaproth read a paper on the gold ores of Transylvania before the Academy of Sciences in Berlin. In his address he reminded his hearers of the forgotten element, and suggested for it the name *tellurium*, meaning *earth*, by which it has ever since been known (*3*). It is hard to understand why so many historians of science credit him with the discovery of tellurium. Klaproth, who was never desirous of undeserved honors, stated definitely that the element had been discovered by Müller von Reichenstein in 1782 (*11*), (*14*).

Klaproth isolated tellurium from the gold ore by the following method. After digesting the pulverized ore with aqua regia, he filtered off the residue and diluted the filtrate slightly with water. When he made the solution alkaline with caustic potash, a white precipitate appeared, but this dissolved in excess alkali, leaving only a brown, flocculent deposit containing gold and hydrous ferric oxide. Klaproth removed this precipitate by filtration and added hydrochloric acid to the filtrate until it was exactly neutral. A copious precipitate appeared. After washing and drying it he stirred it up with oil and introduced the oil paste into a glass retort;

which he gradually heated to redness. When he cooled the apparatus, he found metallic globules of tellurium in the receiver and retort (*3*), (*11*).

The discovery of tellurium was by no means the only service that Müller von Reichenstein performed for the glory of his country. Kaiser Joseph appointed him acting governor (*Gubernialrath*) and raised him to the hereditary nobility with the title of Freiherr (Baron) von Reichenstein. For sixteen years he was a courtier in Vienna, but in 1818 he asked permission to retire. Although he was exempted from making reports, he was still asked to attend all the council meetings, in order that the state might continue to receive his valued advice on mining and metallurgy. The cross of the Order of St. Stephen was awarded to him for distinguished services to his country and he was also elected to membership in the Mining Society, the *Gesellschaft naturforschender Freunde* (Society of Scientific Friends) at Berlin, and in the Mineralogical Society at Jena (*2*). After serving his country for sixty-two years and publishing many contributions to chemistry and mineralogy, Müller von Reichenstein died in Vienna at the venerable age of eighty-five years (*4*).

Courtesy Dr. L. von Szathmáry

PAUL KITAIBEL
1757–1817

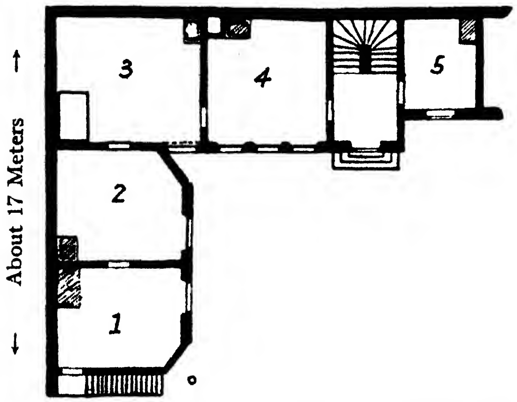
Hungarian chemist and botanist who anticipated Klaproth in his researches on tellurium. The original discoverer of this element, however, was Müller von Reichenstein.

According to Paul Diergart, Paul Kitaibel, professor of botany and chemistry at the University of Pest, discovered tellurium independently in 1789 and wrote a paper on it (*5*), (*14*), (*15*).

Selenium

The discoverer of selenium was no other than the illustrious Swedish chemist, Jöns Jacob Berzelius, who was born in Wäfversunda, a village in

Östergötland, on August 20, 1779. His childhood was saddened by the early death of his parents, but his stepfather provided carefully for his education. After attending the school at Linköping, Berzelius studied medicine at Upsala, and at the age of twenty-two years he received his medical degree. Afzelius, a nephew of Bergman, was then the professor of chemistry, and Ekeberg, who discovered tantalum at about the time of Berzelius' graduation, was an assistant.



SECOND-FLOOR PLAN OF BERZELIUS' LABORATORY AND DWELLING HOUSE

1—Kitchen—Laboratory
2—Laboratory
3—Bedroom
4—Parlor
5—Not used by Berzelius

In the following year Berzelius was appointed assistant professor of medicine, botany, and pharmacy at the celebrated medical school of Stockholm which he served with honor and distinction for the rest of his life. During part of the time he also lectured at the Military College and at the Medico-Surgical Institute at Stockholm. Berzelius, unlike other chemistry professors of his time, enlivened his lectures with many striking demonstrations. His fame as a teacher soon spread throughout Europe, with the result that brilliant ambitious students of chemistry made Stockholm their Mecca. Mitscherlich, Wöhler, C. G. Gmelin, Mosander, Svanberg, Sefström, and the Rose brothers, Heinrich and Gustav, all received their inspiration from the great Swedish master.

A vivid picture of Berzelius and an understanding of his sympathetic attitude toward his students may be obtained by reading the "Early Recollections of a Chemist," by Friedrich Wöhler:

> With a throbbing heart (says Wöhler) I stood before Berzelius's door and rang the bell. A well-dressed, dignified gentleman with florid and healthy complexion let me in. It was Berzelius himself. He welcomed me very cordially, informed me that he had been expecting me for some time, and wished me to tell him of my journey—all this in the German language, with which he was as familiar as with French and English. This first day he took me to the Caroline Institute, where he gave his lectures to medical students, but which were also attended by officers of the army and several of his friends, and which I regularly visited afterwards to accustom my ear to the language. This afforded me opportunity to admire his calm and

clear delivery and his skill in performing experiments. In this institute was also the laboratory for medical students, which was presided over by Mosander (6).

A pencil sketch by Magnus' brother, Eduard. From Hofmann's "Zur Erinnerung an vorangegangene Freunde"

GUSTAV MAGNUS, 1802–1870

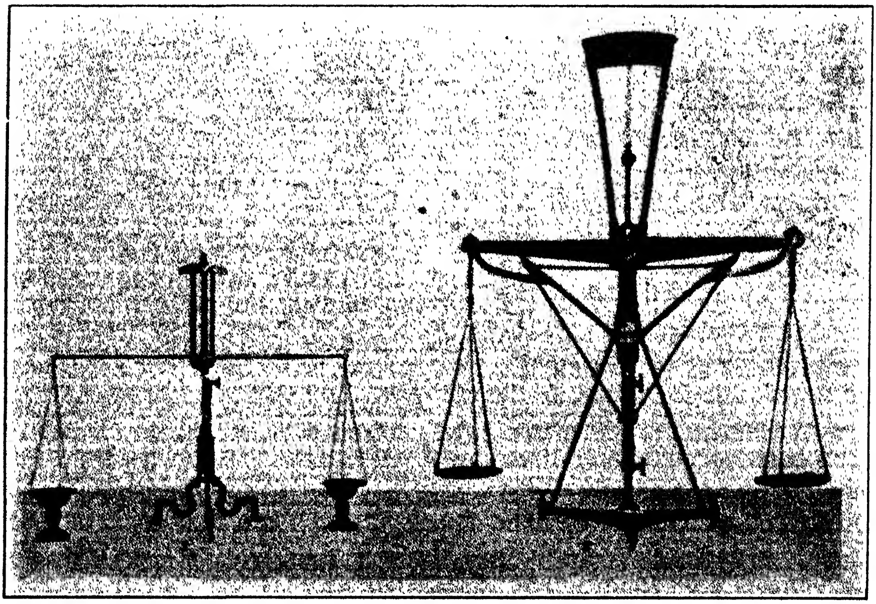
German chemist and physicist. One of Berzelius' distinguished students. He was one of the first chemists to investigate tellurium. He contributed to mineralogical chemical analysis, physiological and agricultural chemistry and chemical technology, and devised a simple process for recovering selenium from the slime in the lead chambers of sulfuric acid plants. He also carried out important researches in mechanics, hydrodynamics, heat, optics, electricity, and magnetism.

Berzelius determined the atomic weights of nearly all the elements then known, and was the first chemist to determine them accurately. He referred his atomic weights to oxygen, which, however, he allowed to equal 100, instead of 16 as in our present system. In his little laboratory that looked like a kitchen and in which the sand-bath on the stove was never allowed to cool, Berzelius discovered the important elements: selenium, silicon, thorium, cerium, and zirconium.

About a hundred miles northwest of Stockholm there lies among barren hills the famous old mining-town of Fahlun. The average tourist might not be greatly interested in the smoky old town with its grimy, little wooden houses, its sickly vegetation, and its odor of sulfuric acid fumes, but the chemist would recall its important rôle in the early history of selenium. Berzelius and Assessor Gahn owned shares in a sulfuric acid plant at Gripsholm that used as raw material pyrite from the mine at Fahlun. On September 23, 1817 (7), Berzelius wrote to his friend, Dr. Marcet of London, that he and Gahn had found tellurium in the sulfuric acid, but on February 6th of the following year he wrote again to Dr. Marcet, telling him that they had been mistaken about the tellurium (8):

> I have just examined it more carefully here at Stockholm (wrote Berzelius) and have found that what Mr. Gahn and I took for tellurium is a new substance, endowed with interesting properties. This substance has the properties of a metal, combined with that of sulfur to such a degree that one would say it is a new kind of sulfur. Here are some of its properties.... If one sublimes it in a large vessel,

> it is deposited in the form of flowers of a cinnabar red, which are nevertheless not oxidized. During its cooling it keeps for some time a certain degree of fluidity, such that one can shape it between the fingers and draw it into threads.... When one heats this new substance with a flame, it burns with an azure blue flame, and gives a very strong odor of radishes; it was this odor that made us think it was tellurium.
>
> The similarity to tellurium has given me occasion to name the new substance selenium.... In the hope of pleasing you and Mr. Wollaston, I am enclosing a little thread of selenium, which will surely be broken before arriving, but some of it will always remain. The paper in which it is wrapped has been colored by a sublimation of selenium which took place when, in my absence, the fire was stirred up too much in order to evaporate a solution of ammonium selenate (*8*).



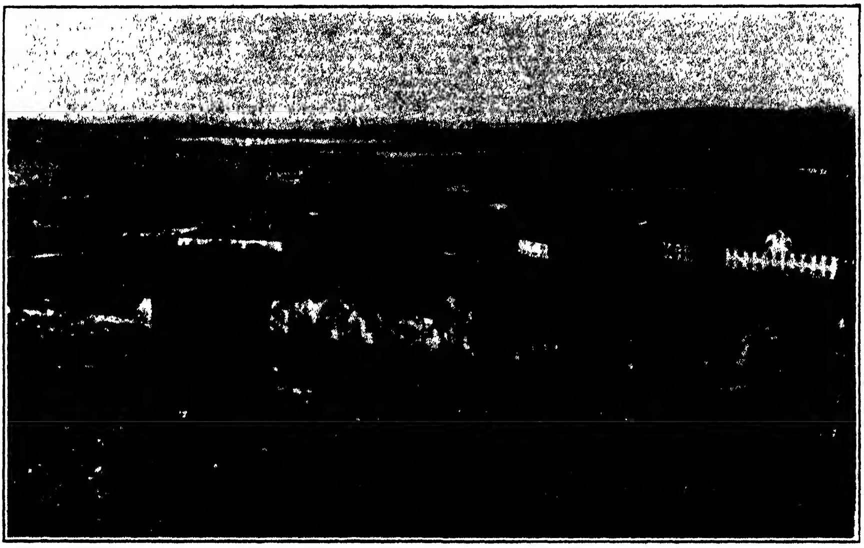
BALANCES USED BY BERZELIUS

The following long quotation from Berzelius not only gives the details of this remarkable discovery, but also serves as a splendid example of his vividly clear literary style:

> They use at Fahlun (he said) for the manufacture of sulfur, pyrites occurring at various places in the copper mine. The pyrites are often mixed with galena, blende, and several foreign substances. The pyrites are placed on a layer of dry wood, in long, horizontal furnaces, the upper part of which is covered with earth and decomposed pyrites; the fumes pass from these furnaces into hori-

zontal tuyeres, the fore part of which is of brick and the rest of wood. The wood is lighted below, and the heat causes the excess sulfur to distil from the lower layer of the pyrite; the gaseous sulfur is carried by the current of warm air, and is finally deposited as flowers in the tuyeres....

When this distilled sulfur is used for manufacturing sulfuric acid by burning it, a red, pulverulent mass is deposited at the bottom of the lead chamber. This fact was observed long ago by Mr. Bjuggren, who then owned a sulfuric acid plant at Gripsholm. He found that this does not occur when another kind of sulfur is used; and as he had learned from a chemist that the red material must contain arsenic, he no longer used sulfur from Fahlun.



From Guinchard's "Sweden," Vol. 2

THE FAHLUN MINE IS THE OLDEST COPPER MINE IN SWEDEN

It was worked in the 13th century, and has been run almost continually ever since. Its present output of copper is small, but iron pyrite is still produced. The pyrite from this mine was the first source of selenium. Gahn, the discoverer of manganese, and Sefström, the discoverer of vanadium, lived in Fahlun.

Since this plant has been purchased by Gahn, Eggertz and myself (continued Berzelius), the Fahlun sulfur has been burned there continually. The red sediment which forms in the acid liquid always remained at the bottom of the chamber, and consequently increased in thickness to the depth of a millimeter. The operation by which the sulfur is acidified in this plant differs from that usually employed in that the sulfur is not mixed with potassium nitrate. Flat glass vessels containing nitric acid are placed on the bottom of the tank and the sulfurous acid gas, in decomposing the nitric acid, produces the nitrous gas necessary for the complete acidification of the sulfur....

Berzelius then explained how he and Assessor Gahn had been misled into thinking that they had found tellurium in the sulfuric acid:

> In the glass vessels containing the nitric acid (said he) there is found, after the complete decomposition of the nitric acid, a concentrated sulfuric acid at the bottom of which is deposited a red, or sometimes brown, powder. This powder aroused our attention and led us to make a special examination of it. The quantity resulting from the combustion of 250 kilos of sulfur did not exceed 3 grams. The principal mass was sulfur; it could be lighted and burned like this substance; but it left a copious ash which, when heated with a blowpipe, gave a strong odor of decayed radishes or cabbage, analogous to that which Klaproth says is produced when one treats tellurium in the same manner. .
>
> The appearance of a substance as rare as tellurium in the Fahlun sulfur led me to try to isolate it, in order to obtain more exact and certain ideas regarding it. I therefore had the whole mass at the bottom of the lead chamber removed. While still wet it had a reddish color, which, upon desiccation, became almost yellow. It weighed about four pounds. It was treated with aqua regia added in sufficient quantity to render the mass pulpy, and was finally digested at a moderate temperature. It gradually changed color, the red disappeared, and the mass became greenish yellow. After 48 hours of digestion, water and sulfuric acid were added, and it was filtered. The filtrate had a deep yellow color. The mass remaining on the filter had not visibly diminished in volume; it consisted principally of sulfur mixed with lead sulfate and other impurities.

ALEXANDER MARCET
1770–1822

Swiss physician and chemist. Lecturer on chemistry at Guy's Hospital, London. Friend of Berzelius, Wollaston, and Tennant. He carried out a number of researches in physiological chemistry. In collaboration with Berzelius he studied the properties of carbon bisulfide.

The final steps in the isolation of the new element were described by Berzelius as follows:

> A small quantity of filtrate (said he) was taken to study the method of separating the substance supposed to be present; it was precipitated with ammonium hydroxide. The precipitate, well washed and dried, mixed with potassium and heated at the end of a barometer tube, decomposed with ignition. Placed in water, a part dissolved, and the liquid acquired the orange color of strong beer, very different

> from the red wine color given by the hydrotelluride of potassium. The liquid did not cover the silvery pellet which always rises to the surface of the hydrotelluride of potassium; but after a few hours, it became turbid and deposited red flakes, the quantity of which was increased by the addition of nitric acid. The precipitate was preserved, and when a part of the filter on which the red precipitate had been collected was lighted at a candle flame, it gave the edges of the flame an azure blue color, meanwhile exhaling a strong odor of putrid cabbage. A portion of very pure tellurium, precipitated in the same manner from a solution of the hydrotelluride of potassium, had a gray color, gave a greenish color to the edge of the flame, and produced no perceptible radish odor. . . .

Berzelius then proved that the odor of impure tellurium is caused by the presence in it of small amounts of the new substance:

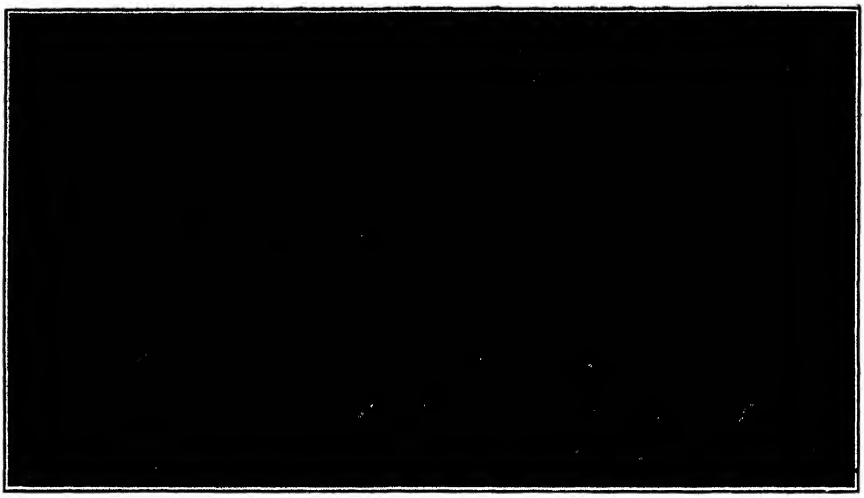
> Upon examining more carefully the purified tellurium which served for my earlier experiments with the oxide of tellurium and hydrogen telluride gas (said he) I found that it produced no odor, either when one heated it with the blowpipe or upon reduction to the oxide, and that the only way to make it produce such an odor was to heat it in a glass tube closed with the finger, until the vaporized metal escaped through a hole in the softened glass. It then burned in this hole with a blue flame, giving an odor entirely analogous to that of the red substance. . . . These experiments seemed to me to prove that the red substance could not be tellurium, but that tellurium itself contains varying amounts of it according to the care with which it has been purified. . . .

Berzelius continued his experiments and soon realized that he was dealing with a new element:

> The brown material, insoluble in water, examined more carefully (said he), was recognized to be the cause of the peculiar odor we mentioned above; and by means of some experiments which we shall report soon, it was found that it was a combustible, elementary substance hitherto unknown, to which I have given the name selenium, derived from Selene (the moon), to recall its analogy with tellurium. According to its chemical properties, this substance belongs between sulfur and tellurium, although it has more properties in common with sulfur than with tellurium *(9)*, *(17)*.

Since Klaproth had named tellurium for the earth, Berzelius thought it appropriate to name the sister element for the earth's satellite. The results of his investigation of selenium and its compounds were published in 1818 in the *Annales de Chimie et de Physique*.

His "*Lehrbuch der Chemie*" was translated into German by Wöhler and was later translated into several other languages. Berzelius also published each year, beginning in 1821, a report on progress in physics and chemistry called the "*Jahresbericht über die Fortschritte in der Physik und Chemie*."



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BERZELIUS AUTOGRAPH LETTER

Translation of Letter, Part of Which Is Reproduced Above

Letter of Introduction written by Berzelius for Mr. Engelke to Herr E. L. Schubarth Ph.D., M.D., Professor Extraordinary of Chemistry at the University of Berlin and Teacher of Chemistry at the Technical Institute in Berlin.

Stockholm, Apr. 14, 1815.

Dear Sir:

I herewith take the liberty to commend to you heartily Mr. Engelke, the bearer of this letter. Mr. Engelke is, to be sure, really neither a scientist nor a technologist; he is employed, however, in our local Commercial College, where, because of exceptional general knowledge and great eagerness to fulfil his duties properly, he will in time take a higher place. The object of his present journey is to study the various industries in foreign countries from the point of view of political economy, and indeed I could recommend him to no other than yourself with greater hope that he would receive sound guidance in these things. I should therefore deem it a great favor if you would have the kindness to receive my friend Engelke so that he may have an opportunity to see and learn the things corresponding to the purpose of his journey.

I beg you to give my best regards to [*name illegible*] and, if there is an opportunity, to introduce Mr. Engelke to him.

With most profound respect, I have the honor to remain, Sir,

Your humble servant, JAC. BERZELIUS

His students and friends adored him. Although Friedrich Wöhler spent only a few months in Stockholm, his contact with the great master influenced the whole course of his life. Their frequent exchange of intimate letters lasted many years, to be interrupted at last only by the death of Berzelius. Berzelius' correspondence with Dr. Marcet, Davy, Wollaston, and others was also extensive.

He did not marry until late in life. On January 29, 1836, he wrote, "Yes, my dear Wöhler, I have now been a benedict for six weeks. I have learned to know a side of life of which I formerly had a false conception or none at all" (*10*). The bride was more than thirty years younger than Berzelius, but their married life proved to be most happy. On the wedding day King Charles Jean of Sweden honored him in a gracious and appropriate manner. As Berzelius entered his bride's home just before the ceremony, his father-in-law handed him a letter, saying that the King wished to have it read aloud to the guests. The letter, which was written in French, announced that Berzelius, because of his eminent services to Sweden, was to be given the dignity and title of Baron (*10*), (*16*).

JÖNS JACOB BERZELIUS
1779–1848

Professor of chemistry and medicine at the Stockholm Medical School. He determined the atomic weights of most of the elements then known, and discovered selenium and the earth ceria, and isolated silicon, thorium, and zirconium. Among his students may be mentioned Wöhler, Heinrich and Gustav Rose, Mosander, Sefström, and Arfwedson.

Selenium is now used instead of manganese for decolorizing glass, and its principal uses are in the glass and ceramics industry. The metallic form of the element is a non-conductor of electricity in the dark, but has a conductivity proportional to the intensity of the light falling on it. This peculiar behavior made possible the construction of the very sensitive photoelectric selenium cell. The first photophone using such a cell for transmitting speech by means of a beam of light was devised by Alexander Graham Bell in 1880. Although modern sound films are made with photoelectric cells of the alkali metal type, the early development of talking pictures, phototelegraphy, and television owed much to the element that Berzelius discovered in the slime of his sulfuric acid plant (*12*), (*13*).

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X. THE KLAPROTH-KITAIBEL CORRESPONDENCE ON THE DISCOVERY OF TELLURIUM

Some letters of Klaproth and Kitaibel which have been carefully preserved in the Hungarian National Museum at Budapest for more than a century shed new light on the early history of the element tellurium and reveal the characters of Baron Franz Joseph Müller von Reichenstein, who discovered it in the gold ores of Transylvania, of Paul Kitaibel, who rediscovered it, and of Martin Heinrich Klaproth, who named it and made it known to the scientific world. Since Professor Ladislaus von Szathmáry's excellent articles (1) on this subject are in the Hungarian language and not readily accessible to most chemists, an English translation of the Klaproth-Kitaibel correspondence is presented here. The original letters of both are in German.

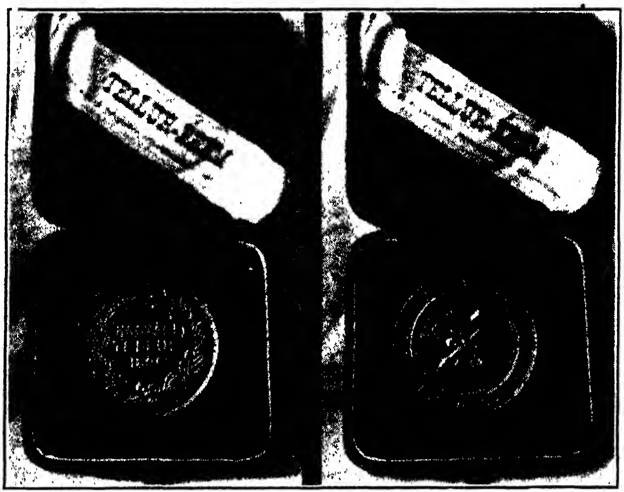
. . . .

The gold mines of Nagyág were discovered by accident. A Roumanian peasant, Juon Armenian (or Armindján), who used to pasture his pig in the Nagyág forest, reported to Baron Ignaz von Born's father that he had seen flames breaking through a crevice, which had led him to believe that there must be a rich deposit of metal there. After years of searching, Born found a black, leafy ore which he at first mistook for pyrite but which proved to be rich in gold. He and his partner, Wildburg, opened the shaft on April 8, 1747, and named it the "Conception of Maria"; the Roumanians, however, called it the "Gypsy Shaft," for a Gypsy who lived nearby used to repair the miners' tools. Although the Born family had no difficulty in extracting the gold, they were unable to determine the composition of the ore, which, because of its rarity, was highly prized by collectors. This ore was found also at Zalatna and Offenbánya, and later in the Börzsöny Mountains (*1*).

In the latter part of the eighteenth century, a skilful Hungarian chemist, Colonel Joseph Ramacsaházy, examined the gold ores of the Börzsöny Mountains and was hampered in his analyses by the presence of a troublesome unknown substance. In describing this ore he used the alchemistic term "unripe gold," and on January 30, 1781, he made a contract with another chemist, Matthew Böhm, to "ripen" it. Böhm deceived him, however, and was deported from Hungary. (This information was generously contributed by Professor von Szathmáry, who obtained it from the Record Office in Budapest.)

At the Maria Loretto shaft near Zalatna in the Facebaj Mountains (lower Fejér County), another white, leafy gold ore known as *Spiessglaskönig* or *argent molybdique* presented similar difficulties. When Professor Anton von Rupprecht of Selmeczbánya (Schemnitz) roasted the mineral gently on charcoal, he found that the metallic residue, when treated with mercury, gave no trace of vermilion (red mercuric sulfide). Since the mineral had a metallic luster, gave no test for sulfur, and behaved in many respects like antimony, von Rupprecht concluded that it must be native antimony.

This view, however, was opposed by a distinguished contemporary. Baron Franz Joseph Müller von Reichenstein was born at Nagyszeben (Sibiu, or Hermannstadt) in the Transylvanian Alps on July 1, 1740.* After receiving his elementary education in his native city, he went to Vienna to study philosophy and law. Later he became so deeply interested in mining, metallurgy, and chemistry that in 1763 he entered the famous School of Mines of Selmeczbánya, or Schemnitz (which is now known as Štiavnica Baňská, Czechoslovakia). Here he studied under the capable leadership of N. J. Jacquin (*1*).



Courtesy Prof. L. von Szathmáry

TELLURIUM MEDALLION

A very rare tellurium medallion bearing on one side the inscription "Tellurium from Nagyág, 1896" and on the other the words "Royal Hungarian smelter at Selmeczbánya [Schemnitz]." The diameter is 43 mm., the thickness 5.5 mm. One of these medallions is owned by the Hungarian National Museum, another by the University of Sopron [Ödenburg].

Upon returning to Transylvania, he served on a mining commission to reorganize the neglected mines of his native country, and later became director of mines in the Banat. When he succeeded in putting the mines on a paying basis, Maria Theresia entrusted him with similar responsibilities in the Tyrol. In 1775, although successfully established as a mining

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* This statement may serve as a correction to page 65 of the first and second editions of "The Discovery of the Elements." Dr. Speter and Professor von Szathmáry kindly informed me that Baron von Reichenstein was born in Nagyszeben, not in Vienna, and that he at first mistook the tellurium not for antimony but for bismuth.

official in the little Tyrolian town of Schwatz, he preferred to return to his own country. King Joseph II gratified this desire by sending him to Transylvania on special commissions, and in 1778 appointed him as provincial commissioner.

During his travels Müller amassed a splendid mineral collection, which he arranged according to Born's system. When he set to work in his poorly equipped laboratory at Nagyszeben to examine the ore which von Rupprecht believed to be native antimony, he made slow progress. On September 21, 1782, however, he published a statement (*2*) to the effect that the mineral in question was not native antimony, but bismuth sulfide. When the ore was melted with niter and tartaric acid, it did not yield antimony. It colored the flame blue and formed an amalgam with mercury, whereas antimony would have failed to give these reactions.

Courtesy Prof. L. von Szathmáry

SELENIUM MEDALLION

A selenium medallion bearing a portrait of Berzelius. The diameter is about 45 mm. This medallion was cast at the Selmeczbánya smelter and is now in possession of the University of Sopron. It is extremely rare and has unfortunately been broken.

In the following year, however, he concluded that the mineral contained neither bismuth sulfide nor antimony, that the gold was an essential constituent of it, and that it contained an unknown metal. In an investigation lasting three years and consisting of more than fifty tests, he determined the specific gravity of the mineral and noted the radish odor of the white smoke which passed off when the new metal was heated, the red color which the metal imparts to sulfuric acid, and the black precipitate which this solution gives when diluted with water (*3*).

Müller also sent a very small specimen of the new substance to Torbern Bergman, who regularly corresponded with him and whom he considered to be "the greatest chemist of the present century." In the reply dated April 13, 1784, Bergman confirmed Müller's results, mentioned Elhuyar's recent discovery of tungsten, commented on the surprising increase in the number of known metals, and added, "I am waiting impatiently for your parcel so that I may work with larger amounts." Unfortunately, Bergman was never able to work with this larger specimen; for he died in July of the same year. Twelve years later, Müller, desirous of still further verification, sent a specimen to Martin Heinrich Klaproth, the leading analytical chemist of Germany, who analyzed it and completely confirmed the discovery of the new metal (*4*). In his report before the Academy of Sciences in Berlin on January 25, 1798, Klaproth named the metal *tellurium* and mentioned that the original discoverer of it was Müller von Reichenstein,

From Szathmáry, "Magyar Alkémisták"

IGNAZ EDLER VON BORN
1742–1791

Distinguished Transylvanian metallurgist, mineralogist, and mining engineer. Kitaibel found tellurium in a mineral which von Born had incorrectly designated as argentiferous molybdenite.

When Müller was promoted to the office of aulic councilor he regretfully left Transylvania for Vienna. He was later pensioned with the order of St. Stephen. He died in Vienna on October 12, 1825 (or 1826?). Although Baron von Reichenstein's wife, Margaretha von Hochengarten, was German, and although he spent much of his life among German people and received many honors from the Austrians, his descendants still live in his native land of Transylvania.

In 1789 the famous Hungarian scientist, Paul Kitaibel, discovered tellurium independently. He was born on February 3, 1757, at Nagy-Márton [Mattersdorf], and attended the academy at Raab in order to prepare himself for the University of Buda. After serving under Professor J. Winterl as adjunct in chemistry and botany (*5*), (*6*), he received his medical degree in 1785.

Four years later young Dr. Kitaibel found a new element in an ore from Deutsch-Pilsen which Baron von Born* had regarded as argentiferous

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* Ignaz Edler von Born (1742–1791). Transylvanian metallurgist. Inventor of a famous amalgamation process of recovering gold and silver.

molybdenite. At the suggestion of Abbé Estner* and Mine Captain Haidinger,† he also investigated the *aurum problematicum* and found that it contained the same new element as that in the molybdic silver. When he sent an account of his researches to Klaproth for criticism, the latter gave a most favorable written report, but evidently gave no further thought to the matter. Müller von Reichenstein later presented Klaproth with his supply of *aurum problematicum*, and Klaproth reported the existence of the new metal, tellurium, *giving full credit to the original discoverer, Müller von Reichenstein*, but failed to mention Kitaibel's work on the "molybdic silver." Since Kitaibel was unaware of the researches of Müller von Reichenstein and had been led to the *erroneous* conclusion that Klaproth had claimed the discovery, he defended his priority over the latter in the following letter to Johann Georg Lenz, professor of mineralogy at Jena (*7*):

> March, 1800.
>
> I received yesterday the diploma which the Mineralogical Society at Jena intended for me and which you were so kind as to send me. I hasten to give you my heartiest thanks and to ask you to express my gratitude to the famous Society for this honor and to assure it that I shall strive to the best of my ability to live up to your mutual aims. At present, to be sure, I am so occupied with the duties of my office, traveling, and botanical work that I scarcely have time to think of other activities, and my field is not so much mineralogy as botany and chemistry; however, since I hope to find much worthy of notice on my trips now about to be taken at public expense, and since the chemical analysis of mineral products not yet sufficiently well known will be no less welcome to the Society than the external characteristics of the same, I yet hope, when time permits, to accomplish some things suited to your aims.
>
> On this occasion I learned that the news has been brought to Jena that I had discovered tellurium before Klaproth and that this famous chemist had appropriated my discovery to himself. The whole matter stands as follows:
>
> About twelve years ago, the professor of natural history, Piller,‡ who died here, gave me a little piece of ore from Deutsch-Pilsen in the Hont region, saying that it was argentiferous molybdenite and that I might determine the silver content. In some experiments that I made with it, I found, to be sure, that it did contain silver (*8*), but it was evident also that the remainder was certainly not molybdenite, but a new metal. After some time, I found the same mineral listed in Born's Catalogue as molybdic silver.
>
> When Abbé Estner came here to appraise the collection of natural history specimens left by Piller, and I learned that this very expert mineralogist was working on a *Mineralogy*, I told him what I had found

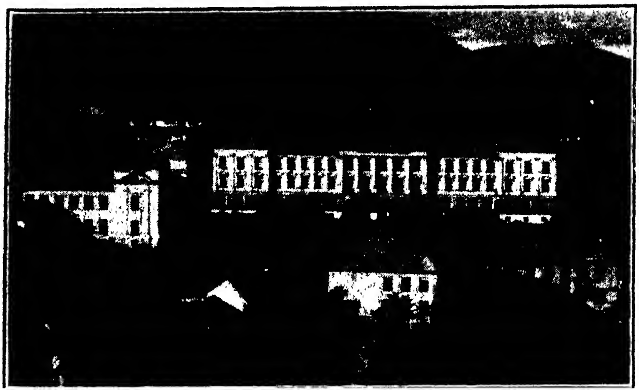
---

* Abbé Franz Joseph Anton Estner (1739–1803). Mineralogist at Vienna.

† Karl Haidinger (1756–1797). Austrian mineralogist and mining engineer. Father of the famous mineralogist, Wilhelm Karl von Haidinger.

‡ Mathias Piller (1733–1788), professor of natural history at Buda.

out experimentally about the so-called molybdic silver and what I believe it to be. At his request, I repeated my previous experiments with the few fragments of this mineral which I still had, compiled [the results], and sent them to him in Vienna. The sagacious mineralogist and Mine Captain Haidinger, who had an opportunity to read my article, wrote me after a time that they believed that the Transylvanian gold ores (*aurum graphicum*, *aurum problematicum*) contain the same metal which I had found in Born's molybdic silver; I wished to investigate the matter more thoroughly and found indeed that the metal which was combined with the gold in the ore possessed all the properties found for that in the ore from Pilsen, which I immediately reported to Abbé Estner.



Courtesy Dr. F. Fiala

THE FORMER SCHOOL OF MINING AND FORESTRY AT SCHEMNITZ, OR SELMECZBÁNYA

Schemnitz, or Štiavnica Baňská, Czechoslovakia, where Müller von Reichenstein, the discoverer of tellurium, was educated. When Austria-Hungary was divided in 1918, the collections, the library, the archives, and most of the portable equipment at the former Schemnitz School of Mines were taken to the University of Sopron in Hungary. Transylvania, with its historic mines of gold and tellurium, became part of Roumania.

Some time after this, Klaproth's analysis of the molybdic silver appeared. To my no slight surprise, I found there the statement that this contains bismuth. Mr. Klaproth then came to Vienna, and Abbé Estner gave him my paper to read, which was returned to me with a very favorable utterance regarding my chemical work. After this, Mr. Klaproth announced his discovery of tellurium. From this it can certainly be surmised with some foundation that this famous chemist was led to this discovery through my work, yet it cannot be proved; and even if the documents which I possess were sufficient for this, yet I would not do it. Mr. Klaproth, with whom I had the honor to become personally acquainted in Berlin a year and a half ago, is my friend, who, it is to be hoped, will himself, when he announces his corrected analysis of the molybdic silver, state to the public that I discovered the aforementioned new metal in this mineral before he did. If he does not do this, Abbé Estner will do it when he comes to this subject in the edition of his *Mineralogy*. Then one may judge from Klaproth's behavior as one will; as long as I shall not have been the cause of it, it will not trouble me. But until then I must ask that no public use of information on this matter, either from my family or from friends, shall be made; the circumstances of my office demand this.

I cherish the hope that some time I may merit your highly desired friendship, and remain, Sir, your most respectful and obedient servant,

K[itaibel].

The following is a translation of the "very favorable utterance" of Klaproth to which Kitaibel referred in the preceding letter:

Courtesy Dr. F. Fiala

"BELHÁZY"

The building at Štiavnica Baňská, Czechoslovakia, which in the eighteenth century housed the chemical and mineralogical laboratories of the former Schemnitz School of Mines. Müller von Reichenstein, the discoverer of tellurium, and A. M. del Río, the discoverer of vanadium, both attended this school.

Vienna, Aug. 1, 1796.

I have read both of the present chemical articles which Abbé Estner kindly communicated to me with so much the greater pleasure because these give praiseworthy evidence that the author of them is a thoroughly practical chemist. The first of these, concerning molybdic silver, is not, to be sure, in entire agreement with my results; but this is easily explained, for my results for these constituents refer only to the individual specimen which I analyzed. . .

Klaproth.

[The portion of the report here omitted refers to Kitaibel's paper on hydroferrocyanic acid and Prussian blue.]

One day as Klaproth was reading Wieland's *New German Mercury*, he ran across the following disconcerting statement (*9*):

> The discovery of the new metal tellurium, which has already, in the first volume of the *Zeitschrift für Ungarn*, been claimed by Professor von Schedius* for our energetic fellow-countryman *Kitaibel* (adjunct at the Hungarian University at Pest) will also soon be claimed for Mr. Kitaibel in the second volume of the *Annalen der Jenaischen Gesellschaft für die gesammte Mineralogie.* Mr. Klaproth in Berlin, who has hitherto been regarded in Germany as the discoverer, was merely led by some of Kitaibel's articles which he read on a visit to Vienna to the further investigation of the new metal, which he named tellurium. Suum cuique!

As a result of this unjust accusation, Klaproth wrote to Kitaibel as follows:

> Berlin Sept. 2, 1803.
>
> Highly esteemed Colleague: It gives me special pleasure to address you by this title, for on February 22nd of this year the Society of Scientific Friends of this place elected you as a foreign member. The sending of the diploma has up to the present been delayed merely because Professor Willdenow,† who is taking charge of it, wishes to include a few books at the same time. In the meantime, they are ready, as Count von Waldstein‡ has noted in the preface to Volume 4B of our *New Publications.*
>
> In proportion as this occasion, like all other opportunities for friendly correspondence with foreign friends and members of our Society has been pleasant and welcome to me, just so deeply do I regret that this my first letter to you also concerns at the same time an unpleasant matter. Only within the last few days have I seen the fourth issue for 1803 of Wieland's *New German Mercury,* in which, to my greatest astonishment, I find myself accused, under the heading: "Further News of Hungary's Most Recent Literature and Culture," of downright theft; in other words, of having robbed you of the discovery of tellurium!! You, my dear colleague, will understand that I can by no means allow this insult to my honor and staining of my reputation to pass unnoticed.
>
> To be sure, I do remember that a chemical paper was handed to me in Vienna with the request for my opinion of it, which resulted favorably. However, as far as the subject matter of it is concerned, this I have completely forgotten, and the person who could inform me is Estner, who is now dead. But, on my honor, and by all that an honest man holds sacred, I assure you that that paper did not have the slightest influence on my chemical experiment with tellurium.
>
> Long before my trip to Vienna, I had worked on this investigation, using a specimen which had been sent here by the late Mr. von Fichtel§ to Mr. Siegfried||; I am also indebted to Mr. Müller von

---

* Ludwig von Schedius (1768–1847). Hungarian writer, editor, cartographer, and humanitarian.

† Karl Ludwig Willdenow (1765–1812). German botanist who studied chemistry under Klaproth.

‡ Franz de Paula Adam Graf von Waldstein (1759–1823). Austrian botanist and philanthropist.

§ Johann Ehrenreich von Fichtel (1732–1795). Hungarian mineralogist.

|| Friedrich Wilhelm Siegfried (1734–1809). German mineralogist.

Reichenstein, who was then in Zalathna, for voluntarily sending me his supply of tellurium ores, which enabled me to carry my earlier investigations farther.

I urgently request and expect a prompt and obliging reply in order to learn whether you yourself will be so good as to arrange that a *public denial* of this accusation of plagiarism made against me may be made as soon as possible; which I shall regard as valuable evidence, not so much of your own love of truth, which I by no means question, as of your friendly and fraternal attitude toward me.

With the best regards of all the regular members of our Society, I have the honor to be, Sir,

Your obedient friend and colleague,
(Signed) Klaproth.
Royal Chief Counselor of Medicine and Sanitation

Kitaibel replied as follows:

Sept. 19, 1803.

Highly Esteemed Colleague:

I received your letter [of September 2nd, 1803] only day before yesterday. Pleased though I was at first to see your esteemed name signed to it, yet all the more deeply was I disconcerted over the real occasion for it: partly because I now truly believe that you have been unjustly insulted; partly because your demand places me in an embarrassing situation from which I do not know how to extricate myself. In order to enable you yourself to judge of this matter and of what can be done to ease your mind, I must make you better acquainted with all the details, which perhaps you do not yet correctly know.

I discovered tellurium in 1789 in Born's so-called molybdic silver. The following year I mentioned it verbally to Mr. Estner and after some time sent him at his request a written article on the experiments I had made with this metal. He and Mine Captain Haidinger expressed to me the opinion that the metal I had discovered probably lay hidden also in the [nagyagite] "Transylvanian gray gold" (as Born called the ores containing this tellurium), whereby I was led to find this metal also in the aforementioned ores, of which Estner and Haidinger immediately received notice. The announcement of this discovery was delayed by circumstances which need not be mentioned here.

Then you came to Vienna, obtained from Estner my article on the investigation of the so-called silver molybdenite and another one on hydroferrocyanic acid prepared in the free state, for your opinion, and Estner sent me your written verdict with the information that he had also communicated to you my report on the metal which lay hidden in Transylvanian gold ores and had requested you to investigate the matter further. I rejoiced over this all the more because I had good reason to hope that, when you announced your investigation, you would mention my work.

When I came to Vienna in the following year, your discovery of tellurium was just being read, and Estner said that he was greatly surprised that you had made absolutely no mention of my report which had been communicated to you. It was also mentioned in presence of others, wherefrom I suspected no consequences whatever. After a long time I was also questioned verbally about the details of the affair, and a foreigner also sent me a written inquiry. Without knowing how they had learned of the matter, I answered according to my knowledge and belief. I now see, to be sure, that it would have been better if I had suppressed what I knew; but you see, too, that we were both wrong, you, in that you did not mention what you had learned of my discoveries through Mr. Estner; and I, in that I mentioned what I knew.

You will understand that it is now difficult to set matters right. I cannot say that you knew nothing of my experiments; my article dated by Estner, your written statement, and Estner's letter prove the contrary. If you were to say that you had forgotten about it and had already made the discovery earlier, I and many others would not doubt it, but this would not sufficiently vindicate you before all men; although no one would have doubted your discovery if you had previously said that you had made it before your trip to Vienna. If I were to say that the details of the matter were other than what I have just written, and which are already known, I would be contradicting myself and speaking falsely.

Under such circumstances I do not know what you mean by a *public denial* which you demand of me. I can give you a statement that my two papers. . .which Abbé Estner gave you in Vienna for your verdict were not concerned with the tellurium of the Transylvanian gold ore but with Born's molybdic silver and free hydroferrocyanic acid; I can add that I believe that you discovered tellurium without knowing anything about my researches, if that will satisfy you. If you can with justice demand more, I ask you to mention it and you will always find. .me ready to do everything which your honor demands and mine permits, for I willingly believe you. That you forgot the contents of my paper, that you discovered tellurium without knowing anything about this, and that, although the premises are true and give cause for detrimental consequences, you were unjustly insulted.

I remain, however, with best regards, Sir,

Your devoted and respectful friend,
K[itaibel]

Klaproth replied as follows:

Berlin, Oct. 4, 1803.

Highly esteemed Colleague:

I am greatly indebted to you for your obligingly prompt reply to my last letter. I must confess, however, that its contents by no means fulfilled my expectations as completely as I had hoped. In the meantime I ask you to pardon me if I am wrong [in believing] that there still remains in your mind some doubt as to the truth of my explanation: *that the article which Estner communicated to me in Vienna has not had the slightest influence on my experiments with tellurium.* Only now does your present letter recall to my mind that I have been concerned with the subject of molybdic silver; but, as regards what you said about it, even at this moment I remember not a single syllable, and I all the more regret that you did not publish this work of yours long ago. I boldly and confidently ask all my friends, here and abroad, who know me better, if it is in any way compatible with my character to be a plagiarist and if they cannot attest on the contrary that discoveries which belong to me have reached the public through others, without my being able to claim them. Yes, indeed. Even today I would rather have made a dozen fewer discoveries than to bear for a moment the slightest suspicion that I could seize the literary property of others.

I believe I have already mentioned in my preceding letter that, several years before my trip to Vienna, perhaps in 1785 to 1786, I had already worked with the so-called *auro problematico* which the late Mr. von Fichtel had sent here to my honored friend, Treasurer Siegfried, and that I was guided by the experiments which Mr. Müller von Reichenstein had made and had described in the *Physical Researches*, and whose belief that it contains a new metal I found to be well grounded; to which conclusion the beautiful criterion previously announced by M. v. R., the red color which this metal imparts to sulfuric acid, was also of special value. Several of my friends here and members of my audience at that time can and will testify to this.

Now just what have I done? Nothing, except to carry out a few little experiments in addition to those published by Mr. M. v. R. on the ore which he himself supplied. But I must almost surmise that you have not seen my complete paper on tellurium. Otherwise you could not possibly retain the *error* that I... [have claimed] the discovery. Nowhere have I said that; on the contrary, I have expressly and emphatically explained that the credit for the discovery belongs to Mr. Müller von Reichenstein. Can one more definitely observe the *suum cuique?* Now since I have never claimed the discovery, it is now as clear as day that I cannot have robbed anyone of this honor. I shall now leave it to you, esteemed colleague, as to what course you may deem best to give complete satisfaction as soon as possible for my publicly insulted honor which, to this day, suffers blamelessly, without compelling me to appear in my own defense; for I hate scholastic feuds like sin. If this be done to my satisfaction, as I have occasion to hope that it will, it will incomparably increase my esteem and respect for you as a friend and colleague whose zeal and services in one of the most beautiful branches of natural science I gladly recognize and honor.

With highest esteem, I remain, Sir,

Your obedient friend and colleague,
(Signed) Klaproth

Thoroughly convinced of Klaproth's integrity, Kitaibel promptly published the following explanation (*10*): (Since the circumstances which gave rise to the unjust charge against Klaproth were stated in detail in the preceding letters, they may be omitted here).

Pest, Oct. 18, 1803.

...The correct conclusion to be drawn really amounts to this: that I discovered tellurium in a misunderstood and hitherto uncertain ore at a time when the individuality of this metal and its existence in the Transylvanian gold ores had not been publicly confirmed through the excellent researches of Mr. Klaproth, and more than this I did not wish to claim for myself, as can be seen from the *Zeitschrift von und für Un-*

> *garn*, volume 1, page 275 ff. For Mr. Klaproth has himself pointed out in volume 3, page 16 of his *Beyträge* that the credit for the original discovery of tellurium belongs to Mr. Müller von Reichenstein, aulic counselor [Hofrath].
>
> However, further inferences have been made and conclusions drawn from the aforementioned circumstances that Mr. Klaproth had borrowed from me the discovery of tellurium, which I hereby declare on the following grounds to be highly unjust and false: In the first place, Mr. Klaproth's blameless character is a security that he, who had no need for such a despicable means of increasing his great deserts and his most widespread renown, was incapable of any such action; in the second place, his researches on tellurium and tellurium ores are so extensive that they could not have been carried out so completely in the short time in which they appeared after his departure from Vienna; in the third place, there is considerable difference between Mr. Klaproth's researches and my own, not only in the success of a few experiments, but also in the completeness of their execution. I found, for example, that tellurium is precipitated from nitric acid by water and that the concentrated sulfuric acid from this metal becomes at first brown, then red, and finally, after continued heating, becomes colorless again. Mr. Klaproth's investigation, on the contrary, left mine far behind in completeness, hence the two cannot be compared; finally, Mr. Klaproth could certainly not borrow from me a discovery which belongs neither to him nor to me (NB. For [the statement]: "Mr. Klaproth has himself already pointed out in volume 3, page 16 of his *Beyträge* that the credit for the original discovery of tellurium belongs to Mr. Müller von Reichenstein, aulic counselor" has been mentioned here on page 461!), as Abbé Eder* has so correctly observed in the *Zeitschrift von und für Ungarn*, volume 2, page 90.
>
> Paul Kitaibel, Professor.

Professor Kitaibel's love for botany was stimulated by his opportunity to arrange the rich herbarium of Counselor Mygind, a friend of Linné. In 1793, after a scientific tour of Croatia, he returned to Pest to join the staff of the school of pharmacy. After managing the botanical garden for a time, he became a professor of botany and chemistry, giving no lectures, however, but spending most of his time on scientific expeditions. In 1795 and 1796 he studied the chalybeate spring at Bardiov [Bartfeld, or Bártfa] and the flora of the Carpathians, and with Count Franz Adam von Waldstein explored the territory around the Sea of Marmora. On a visit to Berlin he met Willdenow, who later named a genus of malvaceæ *Kitaibelia* in his honor. He also explored the beautiful shores of Lake Balaton (the Plattensee, famous for its delicious fish), the fertile Banat, and most of Hungary.

Kitaibel published a number of books and articles on the flora and mineral waters of Hungary, and, according to Professor L. von Szathmáry (*11*), he was the first to prepare solid bleaching powder and use it for bleaching

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* Joseph Karl Eder (1760–1810). Transylvanian historian and mineralogist.

textiles. Kitaibel died at Budapest on December 13, 1817, at the age of sixty-three years; Klaproth's life had come to a close on New Year's Day of the same year. One of their younger contemporaries wrote for the botanical journal *Flora* a memorial article entitled "Some Flowers on the Grave of Paul Kitaibel" (*5*), in which appears the following characterization: "Honest and outspoken, expressing his opinion openly among his friends, and brandishing the lash of the satyrs, he disdained (although sought out because of the kindness of his disposition, the extent of his knowledge, and the force of his intellect) all vain social formalities. . ."

Kitaibel's valuable library was purchased by the National Museum of Budapest, which still treasures the letters which have here been cited. Although this intimate correspondence refers to a disconcerting and embarrassing situation in their lives, it casts no shadow on the reputation of either Klaproth or Kitaibel. Their names, on the contrary, shine all the more brightly today because they refrained from the bitter polemics of the printed page and settled their serious misunderstanding through the exchange of these restrained and courteous letters.

The author is deeply indebted to Dr. Max Speter of Berlin and to Dr. L. von Szathmáry of Budapest for the use of their notes and of the Klaproth-Kitaibel correspondence, for their many gracious and helpful suggestions, and for the reading of the manuscript; and to Dr. František Fiala, director of the State Museum of Mines of Štiavnica Baňská, for his kindness in sending photographs and information regarding the former School of Mines of Schemnitz. It is also a pleasure to acknowledge the assistance received from the Graduate Research Fund of the University of Kansas for translations from the Hungarian, which were made by Mr. Julius Nagy of Chicago.

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(*6*) VON WURZBACH, C., "Biographisches Lexikon des Kaiserthums Oesterreich." Kaiserlich-königliche Hof- und Staatsdruckerei, **1864**, Vol. 11, pp. 337–9. This lexicon also contains biographical sketches of Born, Fichtel, Haidinger, Müller von Reichenstein, Piller, Rupprecht, Schedius, and Waldstein.

(*7*) Döbling, H., "Die Chemie in Jena zur Goethezeit," Gustav Fischer, Jena, **1928**, 220 pp.

(*8*) Klaproth, M. H., "Analytical Essays towards Promoting the Chemical Knowledge of Mineral Substances," Cadell and Davies, London, **1801**, pp. 218–20. (Klaproth found no silver in this ore.)

(*9*) "Fortgesetzte Nachrichten über Ungarns neueste Literatur und Kultur," *Der neue deutsche Merkur*, Stück **4**, 298–9 (1803).

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XI. COLUMBIUM, TANTALUM, AND VANADIUM

Although the metals columbium, tantalum, and vanadium were recognized very early in the nineteenth century, the difficult task of preparing them in a pure state is an achievement of recent years. In 1801 the English chemist, Charles Hatchett, discovered a new element in a specimen of columbite which had an interesting connection with the history of New England. In the same year A. M. del Río, a professor of mineralogy in Mexico, examined some "brown lead from Zimapán," and announced the discovery of a new metal, erythronium. In the following year Berzelius' professor, A. G. Ekeberg, analyzed some tantalite from Finland and found in it an element very similar to Hatchett's columbium. Although Dr. Wollaston believed that columbium and tantalum are identical, Heinrich Rose and Marignac proved that they are two distinct elements. In 1831 Sefström found in some soft iron from Eckersholm a metal, vanadium, which Wöhler proved to be identical with del Río's erythronium.

. . . . . .

> *It is impossible that he who has once imbibed a taste for science can ever abandon it (1).*

Columbium

The element columbium (niobium) was discovered in 1801 by the English chemist, Charles Hatchett,* who was born in London in 1765. As a young man in his thirties he engaged actively in chemical research, and published in the *Philosophical Transactions* an analysis of lead molybdate from Carinthia and the results of some experiments on shell and bone (*2*), and in *Nicholson's Journal* an analysis of an earth from New South Wales called "Sydneia, or Terra Australis" (*31*).

The discovery on which his fame rests was announced before the Royal Society on November 26, 1801 in a paper entitled "Analysis of a Mineral from North America containing a Metal hitherto Unknown" (*3*). This mineral, now known as columbite, is a black rock found in New England, and the specimen Hatchett analyzed had an interesting history.

Edgar Fahs Smith Memorial Collection, University of Pennsylvania

CHARLES HATCHETT, 1765–1847

English chemist and manufacturer. Discoverer of columbium. Most of his researches were in analytical and mineralogical chemistry.

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* See also Chapter XII, pp. 206–24.

Governor John Winthrop the Younger (*30*), (*46*), (*52*) used to take great pleasure in examining minerals, and his manner of collecting them is best described in the quaint words of an early American poet:

Sometimes his wary steps, but
wand'ring too,
Would carry him the Chrystal
Mountains to,
Where Nature locks her Gems,
each costly spark
Mocking the Stars, spher'd in their
Cloisters dark.
Sometimes the Hough, anon the
Gardners Spade
He deigned to use, and tools of th'
Chymick trade (*47*).

On one of these expeditions he may have found in a spring near his home at New London, Connecticut, the rock fragment of columbite which his grandson sent to Sir Hans Sloane (1660–1753) in London, who placed it in the British Museum (*4*).* The specimen had evidently remained in the museum for several decades before Charles Hatchett analyzed it.

From Waters' "A Sketch of the Life of John Winthrop the Younger"

JOHN WINTHROP THE YOUNGER
1606–1676

First governor of Connecticut. Alchemist, manufacturing chemist, and physician. His grandson sent the columbite from which Charles Hatchett later isolated the metal columbium.

Since columbite is a very complex mineral indeed, containing columbic, tantalic, titanic, and tungstic acids, zirconia, thoria, ceria, and yttria, Hatchett must have possessed great analytical ability in order to discover in it the new element, columbium. Although the greatest chemists in Europe held for more than forty years the erroneous opinion that columbium and tantalum are identical, Marignac and Heinrich Rose finally proved that they are two distinct elements. Thus Hatchett was correct in concluding that he had found a new metal in columbite (*53*).

It is to be regretted that a man of such great ability should have given up his scientific research early in life. Thomas Thomson said of him in 1830, " . . . unfortunately this most amiable and accomplished man has been lost to science for more than a quarter of a century; the baneful effects of wealth, and the cares of a lucrative and extensive business having completely weaned him from scientific pursuits" (*5*). In 1845 Berzelius,

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* See Chapter XII.

writing to Wöhler, expressed a similar opinion: "On my previous visit here in Karlsbad," said he, "I made the personal acquaintance of your king as Prince of Cumberland. He asked me if I knew a number of English chemists, and upon my replying that I knew Davy, Wollaston, Tennant, and Marcet, he shook his head and indicated that I had forgotten the foremost one, namely, Hatchett. He seemed greatly pleased that I also knew him, however did not want to believe that he had given up chemistry and become a coach-maker as his father's successor" (*6*). Hatchett retired to his estate at Roehampton, near London, and died at Chelsea on March 10, 1847.

SIR HANS SLOANE, 1660-1753

Founder of the British Museum. Physician, pharmacist, traveler, and collector of books, manuscripts, coins, medals, gems, antiquities, and natural history specimens.

He never succeeded in isolating columbium, and in fact the element eluded chemists for more than six decades. In 1864, however, C. W. Blomstrand reduced columbium chloride by heating it strongly in an atmosphere of hydrogen (*48*), and saw the shining steel-gray metal.

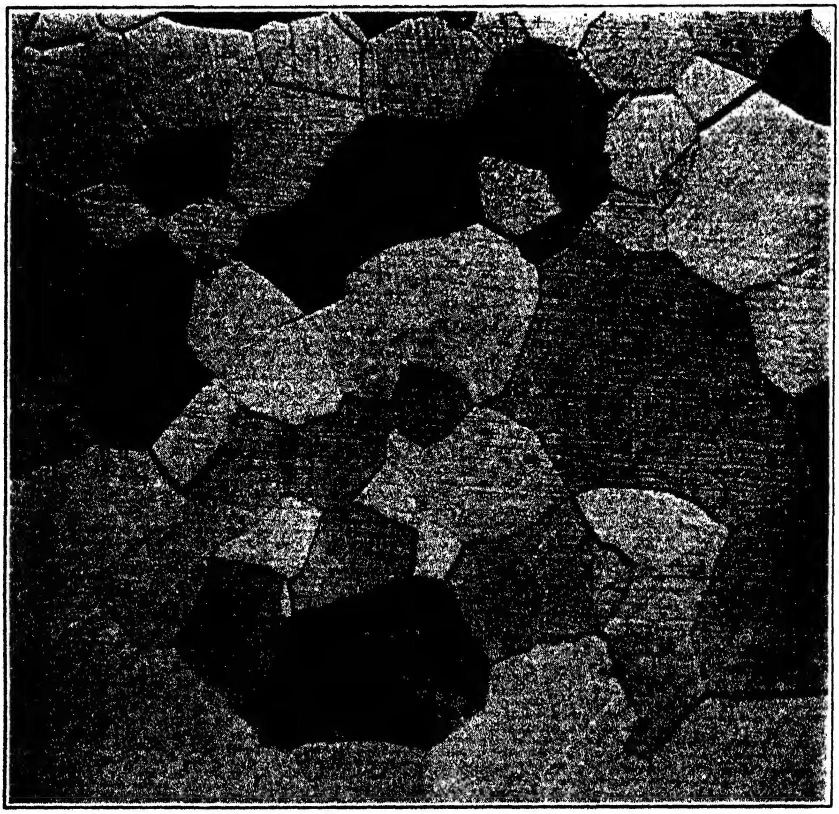
In 1901 Henri Moissan pulverized some American columbite, mixed with it some sugar charcoal, compressed the mixture, and heated it from seven to eight minutes in his electric furnace, using a current of one thousand amperes under fifty volts. After volatilizing all the manganese and part of the iron and silicon, he obtained a melt containing columbium and tantalum combined with carbon.

After preparing columbic acid by Marignac's method, he mixed eighty-two parts of it with eighteen of sugar carbon, moistened the mixture slightly with turpentine, and pressed it into the form of a cylinder, which he heated in his electric furnace, using six hundred amperes under fifty volts. A violent reaction took place in accordance with the equation:

$$Cb_2O_5 + 5C = 2Cb + 5CO.$$

After cooling the mixture out of contact with the nitrogen of the air, he found a well-fused ingot with a metallic fracture (*49*). Moissan's columbium contained a small amount of combined carbon, and was so inert and refractory that he believed the element to be a non-metal resembling boron and silicon.

From 1904 to 1910 C. W. Balke (*7*), (*18*), (*55*) analyzed many columbium and tantalum compounds and determined the atomic weights of both metals. In 1906 Werner von Bolton of the Siemens & Halske Company prepared a columbium regulus by an alumino-thermic method and purified it by repeated melting in a vacuum electric furnace (*17*), (*18*). For twenty-three years this little specimen in Germany continued to be the only piece of pure columbium in the world, but in May, 1929, Dr. Balke exhibited before the American Chemical Society some highly polished sheets and rods of this rare metal. Because less energy is required to remove an electron



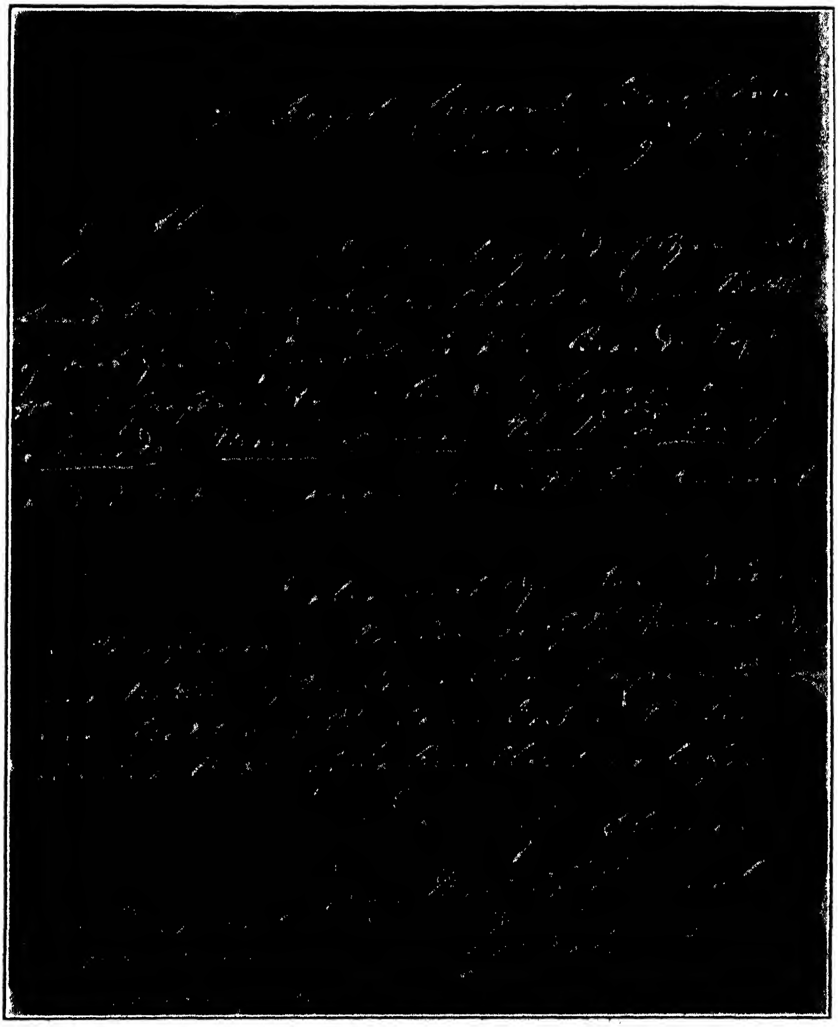
Courtesy Fansteel Products Company, Inc.

PHOTOMICROGRAPH OF COLUMBIUM
Approximately 300×

from its surface than from that of any other refractory metal, columbium is used in vacuum tubes for high-power service (*56*).

Tantalum

Since minerals which contain columbium almost invariably contain also the closely related element, tantalum, it is small wonder that chemists at first confused the two elements. The discoverer of tantalum was the



Edgar F. Smith Memorial Collection, University of Pennsylvania

AUTOGRAPH LETTER OF CHARLES HATCHETT

William Thomas Brande (1788–1866), Davy's successor at the Royal Institution, was Charles Hatchett's son-in-law. The English edition of Brande's "Manual of Chemistry" was dedicated to Hatchett.

Swedish chemist and mineralogist, Anders Gustaf Ekeberg. He was born at Stockholm on January 16, 1767, the son of Joseph Erik Ekeberg, a ship-builder in the service of the King. When he was ten years old he was sent to the school at Kalmar, and two years later he went to Söderokra, where he boarded at the home of the clergyman. It was there that he gained his first knowledge of Greek literature, a subject which gave him great pleasure throughout his life. When he was fourteen years old, he attended school at Westervik and at Carlscrona and was an apt scholar both in science and in art.

He graduated from the University of Upsala in 1788, presenting a thesis on "Oils Extracted from Seeds," and traveled, on salary, through Germany. Soon after his return to Upsala in 1790 he wrote a beautiful poem on the peace recently concluded between Sweden and Russia. In 1794, after publishing his first contribution to chemistry, he began his teaching career at Upsala.

ANDERS GUSTAF EKEBERG
1767–1813

Swedish chemist, mineralogist, poet, and artist. Professor of Chemistry at Upsala when Berzelius was a student there. The discoverer of tantalum. He was one of the first chemists to investigate yttria.

Ekeberg suffered throughout his life from physical handicaps. A severe cold in childhood made him partially deaf for the rest of his life, and in 1801, when a flask exploded in his hand, he lost the sight of one eye (*9*).

When the royal family visited Upsala in November of that year, an elaborate chemical exposition was held in their honor. A poem of three

HENRI MOISSAN, 1852–1907
Professor of Chemistry at the *École de Pharmacie* and at the Sorbonne. The first to isolate fluorine and make a thorough study of its properties. With his electric furnace he prepared artificial diamonds and many rare metals. He brought about a revival of interest in inorganic chemical research.

stanzas, which Ekeberg had composed and written with invisible ink, appeared in blue letters when the King warmed the paper. It began as follows:

> *That in our land the sciences' pure light*
> *Is mingled not with flash and gleam of sword,*
> *Oh Monarch, 'tis thy work. Accept our hearts' oblation.*
> *May we, too, celebrate, with joyous visages,*
> *The long-awaited hour when Peace the world doth greet* (*57*).*

Ekeberg became deeply interested in the wonderful minerals to be found at Ytterby and Fahlun, and made excellent analyses of a number of them. In 1802 he analyzed a specimen of tantalite from Kimito, Finland, and another mineral, yttrotantalite, from Ytterby, and found that both contained a hitherto unknown metal. Because it had been such a tantalizing task to trace it down, Ekeberg named it *tantalum* (*32*).

HEINRICH ROSE, 1795–1864

German analytical chemist and pharmacist. Son of Valentin Rose the Younger. His comparative study of American columbite and Bavarian tantalite proved that columbium (niobium) and tantalum are two distinct metals.

In 1809 Dr. Wollaston analyzed both columbite and tantalite (*10*). His conclusion that columbium and tantalum are identical was accepted by chemists until 1846, when Heinrich Rose (a grandson of Valentin Rose the Elder and son of the Rose whom Klaproth educated) questioned it. Rose had made a thorough study of the columbites and tantalites from America and from Bodenmais, Bavaria, and had extracted from them two acids which he called niobic (columbic) and pelopic acids. He found later, however, that the latter was not the acid of a new metal, as he had at first supposed, but that it contained niobium (columbium) in a lower state of oxidation. Rose stated that niobic and hyponiobic acids are both different from tantalic acid (*11*).

Although columbic and tantalic acids are extremely difficult to separate, Marignac finally succeeded, not only in separating them, but also in show-

---

* *At Wetenskapers rena Dag*
Ej blandades hos oss med blixtarne af swärden,
Det är ditt werk, Monark, vårt hjertas offer tag!
Wi fire, jemwäl wi, med glädjens anletsdrag
Den länge drögda stund, då Freden hälsar werlden.

ing that columbium is both tri- and pentavalent, whereas tantalum always has a valence of five. The separation is based on the insolubility of potassium fluotantalate in comparison with potassium fluo-oxycolumbate (*12*), (*20*). In the United States the element discovered by Hatchett is known as *columbium*, but in Europe most chemists prefer to use the name *niobium* which Heinrich Rose gave it.

Ekeberg's later years were made less fruitful by continued illness. The few papers which he published contained the results of the analyses of minerals such as gadolinite, the topaz, and an ore of titanium. In his analysis of the mineral water of Medevi he was assisted by an obscure young student who was destined to bring great glory to the University of Upsala. The discovery of such a student as Berzelius was a far greater honor for Ekeberg than his disclosure of the rather rare element, tantalum.

Berzelius warmly defended Ekeberg's claim to the discovery of this element. In the autumn of 1814 he wrote to Thomas Thomson objecting to an alteration which had been made in an English translation of one of his memoirs. Berzelius had used the word *tantalum*, and Thomson had evidently substituted the word *columbium*, whereupon Berzelius wrote, "Without wishing to depreciate the merits of the celebrated Hatchett, it is nevertheless necessary to observe that tantalum and its properties in the metallic as well as in its oxidized condition were not known at all before Mr. Ekeberg."

Berzelius went on to explain the differences between Ekeberg's tantalum oxide and the columbium oxide prepared by Hatchett:

> Mr. Ekeberg received from a friend who had visited England [said he], a little portion of the columbic acid of Mr. Hatchett, and when the experiments of Mr. Wollaston came to his knowledge he examined that acid in a scrupulous manner. He recognized in it a large amount of tungstic acid which had given to the oxide its properties of reacting acid as well as those of combining with the alkalies and of coloring microcosmic salt. These observations of Mr. Ekeberg have gained still more weight by the discovery of a new fossil* that Mr. Gahn and I have just made near Fahlun, which fossil possesses the general properties of Mr. Hatchett's columbite, and in the analysis of which we have found oxide of tantalum combined with tungstic acid. . . .
>
> Now, then [continued Berzelius], it is clear that the columbic acid of Mr. Hatchett, having been composed of oxide of tantalum and tungstic acid, which communicated to it a part of its specific properties, it is clear, I say, that Mr. Hatchett shares the discovery of tantalum in almost the same manner as MM. Fourcroy and Vauquelin share with Mr. Tennant the honor of having discovered osmium ("Thomson's System," Ed. IV, Vol. 1, p. 200), and I suppose that you will not refuse to render the same justice to the work of the Swede Ekeberg that you have just rendered to the Englishman Tennant.†

* A tantalite from Broddbo.

† See Part XIV, pp. 256–9.

> As for the name of the metal [said Berzelius], I do not think that the author of the discovery ought to count for much. For example you do not say menaccanite instead of titanium;* moreover Mr. Hatchett gave this name after the place where it was thought the fossil had been found; now it is not good practice to name elementary substances in chemistry after the places where they have first been found; not to mention the fact that the place where columbite was found is still doubtful, in the same degree as it is not certain that it comes from America. The name tantalum having none of these inconveniences and involving a beautiful meaning of a few properties of this particular metallic body, I have felt compelled to choose it by preference. The reason for the name tantalum (derived from the story of Tantalus) is still more valid if one adds that metallic tantalum, reduced to the finest powder, is not attacked by any acid, not even by aqua regia, concentrated and boiling (*13*).

In his reply to this letter on November 5, Thomson explained that he had known very little about Ekeberg's experiments and that his only reason for changing Berzelius' nomenclature had been to make the article more intelligible to English readers. He then added:

> I regret that it never has been in my power to make experiments on either of these substances (columbite or tantalite). Ekeberg supplied me with a good many specimens, but the ship containing them and all my Swedish collection, which I valued highly, was sunk in the Baltic, and all my property lost. Your fact about the new mineral like collumbite (*sic*) is very interesting. I shall insert what you have told me in the next number of my journal. It is all unknown here (*14*).

THOMAS THOMSON, 1773–1852

Scottish chemist and editor. The first distinguished advocate of Dalton's atomic theory. Author of a two-volume "History of Chemistry" characterized by its scientific accuracy and beautiful literary style.

On March 29, 1815, Dr. Marcet wrote to Berzelius:

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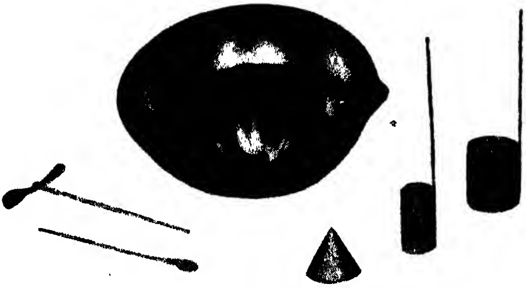
* See Part XVIII, pp. 318–22.

> . . . . Dr. Wollaston made some time ago in my presence a little experimental inquiry on wolfram and tantalite and columbite, by which it appeared that Hatchett's columbite did not contain any tungsten, and that therefore he did not make the mistake you suspected he had made. If you are curious to have the details, I shall send them to you (*15*).

After prolonged suffering with tuberculosis, Ekeberg died at Upsala on February 11, 1813, at the early age of forty-six years. In a letter to Dr. Marcet (*16*), Berzelius paid the following tribute to his gifted teacher: "Ekeberg has just died after a long, sad, hectic illness. He was one of the most lovable of men, he had sound knowledge, and an irresistible propensity for work. He was a good chemist and mineralogist, a good poet and an excellent artist."* Ekeberg had a kind, friendly, merry spirit that frequently soared above poverty and suffering, and his love of literature and art was a constant solace to him.

Tantalum can be separated from columbium by recrystallization of the double potassium fluorides. In the commercial process the ore is fused with caustic soda. The insoluble sodium columbate, sodium tantalate, and iron tantalate are filtered off from the soluble sodium salts, and the iron is removed by treatment with hydrochloric acid. The columbic and tantalic acids are treated with hydrofluoric acid and enough potassium fluoride to convert the tantalum into the double fluoride, K_2TaF_7, which is then recrystallized from water containing a little hydrofluoric acid (*7*).



Courtesy Fansteel Products Company, Inc.

LABORATORY EQUIPMENT MADE FROM TANTALUM

After Werner von Bolton of Charlottenburg succeeded in 1903 in refining the metal, it soon acquired a limited use as filaments (*34*). It was found, moreover, that surgical and dental instruments made from it can be sterilized by heating or by immersion in acids without damage to the tantalum. Since, the price was almost prohibitive, however, Dr. Balke set to work in Chicago to make the metal on a commercial scale. Using as his raw material a rich tantalum ore from the desolate Pilbarra region of western Australia, he finally succeeded in February, 1922, in preparing a tantalum ingot which was passed repeatedly through a rolling mill to produce a flawless piece of sheet metal (*8*), (*19*).

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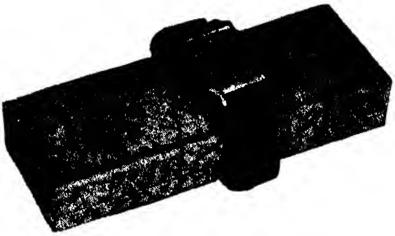
* *"Ekeberg vient de mourir après une maladie hectique longue et malheureuse. Cet homme était des plus aimables; il possédait des connaissances solides et un penchant irrésistible pour le travail. Il était bon chimiste et minéralogue, heureux poëte et très bon peintre."*

Tantalum is now made into spinnerets for the manufacture of rayon, into electrodes for the neon signs that give our Great White Ways a ruddier light, and into fine jewelry with iridescent colors. Its most interesting use, however, depends on its peculiar electrochemical behavior caused by the insolubility of its oxide in acid solutions. When an alternating current is passed through a vessel containing sulfuric acid, a bar of lead and a bar of tantalum (or of columbium), it becomes a direct current (7), (*19*). Thus, because direct current was needed in the early days of radio reception, Ekeberg's tantalizing metal, in the form of radio rectifiers, "B" battery eliminators and trickle chargers, entered into the home life of thousands upon thousands of families.



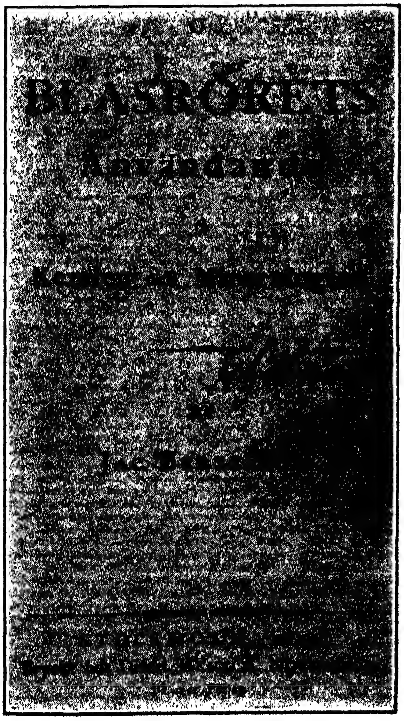
Courtesy Fansteel Products Company, Inc.

TANTALUM FOR WATCH CASES

Vanadium

In 1801, the year in which Hatchett discovered columbium, Andrés Manuel del Río, a professor of mineralogy in Mexico, examined a specimen of brown lead from Zimapán and concluded that it contained a new metal similar to chromium and uranium. Very little has been written concerning the personal life of del Río.* He was born in Madrid on November 10, 1764, studied at Freiberg and at Schemnitz, and finally became a professor in the School of Mines (Colegio de Minería) in Mexico City, where he taught for about fifty years (1795–1849) (*2*), (*50*), (*51*).

It was there that he discovered a new metal which, because of the red color that its salts acquire when heated, he named *erythronium* (*44*). Upon further study, however, he decided that he was mistaken, and that the brown lead from Zimapán was merely a basic lead chromate contain-



BLASRÖRETS

SEFSTRÖM'S AUTOGRAPH ON TITLE PAGE OF BERZELIUS' TREATISE ON THE BLOWPIPE

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* See Chapter XIII, pp. 225–35.

ing 80.72% of lead oxide and 14.80% of chromic acid (*12*). His paper therefore bore the modest title, "Discovery of Chromium in the Brown Lead of Zimapán" (*21*). In 1805 Collet-Descotils confirmed del Río's analysis (*22*), and for twenty-five years no more was heard of the new element, erythronium.

In 1820 del Río went to the Spanish court to plead for Mexican independence. His paper (*1*) on the "Analysis of an alloy of gold and rhodium from the parting house at Mexico" was published in the *Annals of Philosophy* in October, 1825. The closing years of his long useful life were spent in Mexico, where he died on March 23, 1849.

In 1831 the Swedish chemist, Nils Gabriel Sefström, discovered a new element in iron from the Taberg mine in Småland. Sefström was born on June 2, 1787, at Ilsbo Socken, Norra Helsingland (*2*). He studied medicine, and received his medical degree at the age of twenty-six years. After four years of practice in a hospital, he became a professor of chemistry and science at the Caroline Institute of Medicine and Surgery, and from 1820 to 1839 he taught chemistry at the newly erected School of Mines at Fahlun (*2*), (*54*).

It was there that he made the remarkable discovery that Berzelius described so charmingly to Wöhler in his letter of January 22, 1831:

> In regard to the sample which I am sending with this, I want to tell the following anecdote: In the far north there lived in olden times the goddess Vanadis, beautiful and lovable. One day some one knocked at her door. The goddess remained comfortably seated and thought: let the person knock again; but there was no more knocking, and the one who had knocked went down the steps. The goddess was curious to see who it might be that was so indifferent to being admitted, sprang to the window, and looked at the one who was going away. Alas! she said to herself, that's that fellow Wöhler. Well, he surely deserved it; if he had been a little more concerned about it, he would have been admitted. The fellow does not look up to the window once in passing by. . . .
>
> After a few days some one knocked again at the door; but this time the knocking continued. The goddess finally came herself and opened the door. Sefström entered, and from this union vanadium was born. That is the name of the new metal, whose former name suggesting Erian, meaning wool (whence Erianae was educated, since Minerva taught human beings to spin wool), has been rejected. The Herr Professor guessed correctly that the lead mineral from Zimapan contains vanadium and not chro-

NILS GABRIEL SEFSTRÖM
1787–1845

Swedish physician and chemist. Professor at the Caroline Institute of Medicine and Surgery and at the School of Mines in Stockholm. In 1831 he discovered vanadium, an element that proved to be identical with del Río's "erythronium."

> mium. Sefström himself proved with the little specimen belonging to the professor that it is vanadium oxide.
>
> Vanadium [continued Berzelius] is a thing which is very hard to find. It is related to everything with which it forms compounds in definite proportions, even with silica, so that only now have I been able to obtain it pure. In Sefström's vanadium oxide which he brought with him are found phosphoric acid, silica, alumina, zirconia, and ferric oxide, of whose presence we had no suspicion, but which we, because of ambiguous results, had to remove, one after another; so that in the three weeks which Sefström spent in working with me, we confined ourselves almost entirely to the task of finding these impurities and of thinking out ways of removing them. Sefström had to go home, but left me so much vanadium that I have been in no embarrassment over the continuance of the investigation. I shall send the Herr Professor some of it later, when I see about how much I can spare; but now in the midst of the research I need all I have (*23*).

Berzelius then consoled Wöhler for his failure to discover vanadium, saying it required more genius to synthesize urea than to discover ten new elements (*58*). "I have mailed to Poggendorff," he continued, "a little paper on vanadium by Sefström. I have also engaged Sefström to present it to the Academy so that his name alone may be linked with the discovery. which would not be the case if the first paper on it appeared under his and my name together. Thus it also becomes possible to announce the discovery sooner than if we had to wait for the conclusion of my research. which surely cannot be completed so quickly" (*23*).

Two weeks later Wöhler replied:

> A thousand thanks, dear professor, for your kind letter with the beautiful story about the goddess Vanadis, which gave me great pleasure, although, frankly, it vexed me a little, though only at first, to have made no visit to the beautiful one. Even if I had charmed her out of the lead mineral, I would have had only half the honor of discovery, because of the earlier results of del Río on erythronium. But Sefström, because he succeeded by an entirely different method, keeps the honor unshared. As soon as I know the intimate relations of the metal, and you have sent me a little of it, I will analyze the lead mineral. . . .
>
> Anticipatory as it may seem [continued Wöhler] yet, because of the slowness of the mails, it is time to ask whether, when I publish a notice of the mineral, I ought to give its earlier history, the supposed discovery by del Río of a new metal in it, the refutation by Descotils? that Humboldt brought it with him, etc.? I would not want in the least to take away from Sefström anything of his priority of discovery, especially since such indecision is repugnant in cases like this; on the other hand one must not expose one's self to the charge by the public or especially by one's opponents that one through partisanship concealed earlier claims. In any case Humboldt shall be named, since he alone brought it with him, and with that the rest seems unavoidably linked. Do not laugh at me because of my diplomatic question . . . . . (*23*).

The keenness of Wöhler's disappointment is more definitely expressed in his letter to Liebig of January 2, 1831, in which he writes:

> . . . at the moment I am interested only in the new Swedish metal, vanadium, discovered by Sefström, but really by Berzelius. *Ich war ein Esel* not to have discovered it before in the brown lead ore from Zimapan, Mexico. I was engaged in analyzing it and had already found in it something new when, in consequence of hydrogen fluoride vapor, I became ill for several months (*24*).

From Thomas Thomson's "Travels in Sweden During the Autumn of 1812"

TABERG, SMÅLAND, SWEDEN

Sefström discovered vanadium in iron from the Taberg mine.

For a description of Sefström's method of isolating vanadium, it is necessary to quote again from the correspondence of Berzelius, this time from a letter to Dulong. On January 7, 1831, he wrote:

> I must tell you of the discovery of a new metallic substance, of which this letter contains some preparations. . . . The discovery was made by Mr. Sefström, director of the School of Mines at Fahlun, who, wishing to examine a kind of iron remarkable for its extreme softness, found in it, in extremely small quantity, a substance whose properties appear to differ from those of bodies hitherto known, but the quantity of which was so infinitely small that too much expense would have been necessary in order to extract enough of it to permit of

closer examination. This iron was taken from the Taberg mine in Småland, which however contains only traces of the new body, but Mr. Sefström, having found that the cast iron contained more of it than the wrought iron, concluded that the scoria formed during the conversion of the cast iron to malleable iron ought to contain larger quantities of it. This proved to be true. Mr. Sefström extracted portions of it which sufficed for studying it, and during his Christmas vacation came to see me, to finish with me the study of "the stranger (*nouveau débarqué*)" (*25*).

ANDRÉS MANUEL DEL RÍO
1764–1849

Spanish-Mexican scientist. For half a century he was professor of mineralogy at the School of Mines of Mexico.

Sefström's own account of the discovery is also of great interest:

> It is several years [said he], since Rinman, the manager of the mine, in order to discover easily whether an iron was brittle, gave a method which depends on the circumstance that such an iron, when attacked by muriatic (hydrochloric) acid, gives a black powder. Having occasionally treated in this manner an iron which was not brittle, and finally some iron from Eckersholm, I was greatly surprised to recognize in the latter the reaction of a brittle iron, although the iron from Taberg passes for the most flexible and tenacious that we have. I did not then have the leisure to investigate the nature of the black powder; but in April, 1830, I resumed my experiments to see if it contained phosphorus or any other substance, which was for me not without importance.
>
> I dissolved a considerable quantity of iron in muriatic acid [Sefström

> then continued] and I noticed that, while it was dissolving, a few particles of iron, mainly those which deposit the black powder, dissolved more rapidly than the others, in such a way that there remained hollow veins in the midst of the iron bar. Upon examining this black powder, I found silica, iron, alumina, lime, copper, and, among other things, uranium. I could not discover in what condition this substance was, because the small quantity of powder did not exceed two decigrams, and, moreover, more than half of it was silica. After several experiments I saw that it was not chromium, and the comparative tests that I made proved to me that it certainly was not uranium. I had sought to compare the highest degrees of oxidation, but I must remark that vanadium is found partly in the lower degree (*26*).

In one of his letters Berzelius mentioned to Wöhler an unfortunate accident: " . . . As Sefström came home to Fahlun," said he, "to take up there the study of the vanadium alloy, a student spilled about one lot (ten grams) of dissolved vanadium oxide in such a way that none of it could be saved. Now he has nothing with which he can work, and must repeat the entire preparation process on the slag" (*27*).

In May, 1830, a careful comparison of vanadium and uranium was made in Berzelius' laboratory. It was found that vanadium forms two series of compounds, the vanadic and the vanadous, but Berzelius and Sefström did not succeed in isolating the metal. Sefström died at Stockholm on November 30, 1845, at the age of fifty-eight years.

SIR EDWARD (T. E.) THORPE, 1845–1925

English chemist famous for his research on the specific volumes of liquids in relation to their chemical constitution, and for his work on the oxides of phosphorus and the compounds of vanadium done in collaboration with Sir Henry Roscoe. Author of excellent textbooks of chemistry and of biographies and essays in historical chemistry.

Wöhler's researches (*45*) proved that he had been correct in believing that the ore del Río had analyzed in 1801 really contained vanadium instead of chromium (*26*). This mineral is now known as vanadinite, $PbCl_2 \cdot 3Pb_3(VO_4)_2$.

The final step in the discovery of vanadium was accomplished by the English chemist, Sir Henry Enfield Roscoe, who was born in London on January 7, 1833. When he was nine years old the family moved to Liverpool. One of his first schoolmasters reported that "Roscoe is a nice boy, but he looks about him too much, and does not know his irregular verbs" (*36*). His mother, who evidently did not object seriously to this habit of "looking about," encouraged him to make chemical experiments at home and allowed him to transform one of the rooms into a laboratory.

At the age of fifteen years the boy entered University College, London, where he studied under Thomas Graham and Alexander William Williamson. After graduating in 1853 with honors in chemistry, he went to Heidelberg to study quantitative analysis in the old monastery that had been transformed into a laboratory for Bunsen. After passing his doctor's examination *summa cum laude*, he collaborated with Bunsen in the famous researches on the chemical action of light. During their long friendship Roscoe received from the great German master one hundred twenty-six letters, which he carefully preserved and finally presented in bound form to the Bunsen-Gesellschaft (*38*).

When only twenty-four years old, Roscoe succeeded Frankland as professor of chemistry at the University of Manchester. In the winter of 1862, when thousands of employees in the cotton mills of Lancashire were thrown out of work because of the Civil War in America, Roscoe, in an effort to relieve the mental depression of the unemployed, instituted a series of popular "Science Lectures for the People." Roscoe, Tyndall, Huxley, and other noted scientists addressed large and appreciative audiences each week for eleven consecutive winters, and the printed lectures were afterward sold for a penny all over the world (*39*). In his teaching Roscoe emphasized the need of liberal culture as a basis for technical training (*28*).

CARL FRIEDRICH RAMMELSBERG
1813–1899

German chemist, mineralogist, and crystallographer who demonstrated the isomorphism of sulfur and selenium crystals obtained from carbon bisulfide solutions of these elements, and showed that the vanadates are isomorphous with the phosphates. He also determined the crystal forms of many organic compounds, and wrote textbooks on crystallography, metallurgy, and mineralogical and analytical chemistry

In about 1865 he found that some of the copper veins of the Lower Keuper Sandstone of the Trias in Cheshire contained vanadium (*37*) and that one of the lime precipitates from this ore contained about two per cent of it. It was from this unpromising material that Roscoe and Sir Edward Thorpe laboriously prepared the pure vanadium compounds needed for a thorough study of the element.

When Roscoe investigated them he found that vanadium is a tri- and pentavalent element of the phosphorus group. He also discovered that what Berzelius had taken for the metal was really the mononitride, VN, and that most of the vanadium compounds studied by the Swedish chemists had contained oxygen.

On August 26, 1867, Roscoe wrote to Thorpe saying,

> . . . I want you very much to stay with me till April to settle the vanadium and light matters and help me in London with my lectures. . . I have at last found out about vanadium. The acid is V_2O_5 like P_2O_5. The chloride $VOCl_3$ like $POCl_3$ and the solid chlorides $VOCl_2$, VOCl, etc. This explains the isomorphism of the vanadate of lead and the corresponding phosphate and lots of other points. It becomes very interesting now. . . (*40*).

On September 12 of the same year Roscoe wrote again to his assistant:

> Please ask Joseph [Heywood] to send me per book-post *Pogg. Ann.*, vol. 98, in which volume is Rammelsberg's paper on the isomorphism of vanadates and phosphates. There is no doubt in my mind that vanadic acid is V_2O_5, and it will be *exceedingly* interesting to work out the vanadates, which must all be explained as phosphates. The ordinary white NH_3 salt is NH_4VO_3 (like $NaPO_3$) and is a metavanadate. The bi-vanadates can also be explained, but all need re-preparation and analysis. Did I tell you that we have now got V_2O_5, V_2O_4, V_2O_3, V_2O_2 (I wish we had V also!), $V_2O_2Cl_6$, $V_2O_2Cl_4$, $V_2O_2Cl_2$, or $VOCl_3$, $VOCl_2$, VOCl? At St. Andrews I saw Professor Heddle; he has a crystal half apatite and half vanadinite, and he threw out the suggestion long ago that vanadic acid is V_2O_5. . . (*40*).

Five days later he sent Thorpe a detailed report of his experiments on the oxides of vanadium and said in conclusion, "The thing above all others necessary for us now is to get the *metal*" (*40*).

Roscoe's first paper on the subject was the Bakerian Lecture read before the Royal Society on December 19, 1867. On February 14, 1868, with Sir Edward Thorpe as his assistant, he gave a demonstration lecture at the Royal Institution in which he proved that the lemon-colored chloride to which Berzelius had assigned the formula VCl_3 actually contains oxygen. When the audience saw him pass the vapor from a few grams of this chloride, together with pure hydrogen gas, over red-hot carbon, and watched him test the resulting gas for carbon dioxide by passing it into clear baryta water, it was convinced that Berzelius' formula must be incorrect. Roscoe proved by analysis that the lemon-colored chloride is an oxychloride now known as vanadyl chloride, $VOCl_3$ (*12*), (*29*).

When he began his researches on vanadium, its compounds were listed at £35 per ounce, and the metal itself was unknown. After all attempts at direct reduction of the oxides had failed, Roscoe attempted to reduce vanadium dichloride, VCl_2, with hydrogen. Rigorous exclusion of oxygen and moisture was necessary, and, since vanadium metal reacts violently with glass and porcelain, the chloride was placed in platinum boats inside a porcelain tube. The tube itself could not be made of platinum because of the porosity of that metal at red heat.

When he heated the tube, hydrochloric acid gas came off in "torrents," and continued to be evolved in decreasing quantity for from forty to eighty hours. When it finally ceased to come off, the tube was cooled and the boat was found to contain "a light whitish grey-colored powder, perfectly free from chlorine." When Roscoe examined this powder under the microscope, he found that it reflected light powerfully and that it consisted of "a brilliant shining crystalline metallic mass possessing a bright silver-white lustre." Roscoe's paper announcing the isolation of metallic vanadium was read before the Royal Society on June 16, 1869 (*33*).

While studying at Heidelberg, Sir Edward Thorpe read in a French periodical on popular science that the Copley Medal had been awarded to Sir Henry E. Roscoe. His letter of congratulation brought the following reply:

From Thorpe's "The Right Honourable Sir Henry Enfield Roscoe"

SIR HENRY ENFIELD ROSCOE, 1833–1915

Professor of Chemistry at the University of Manchester. Collaborator with Bunsen in researches in photochemistry. Author of excellent textbooks and treatises on pure and applied chemistry.

> In the first place let me thank you for your letter and congratulations upon the great French discovery! Many of these Parisian wonders have after all turned out myths—and this last is, I believe, no exception—the expression "Medaille de Copley" is, so far as I am aware, the French (and bad French, too!) for the "Bakerian Lecture." I am, however, none the less obliged to you for your good wishes on this occasion, and for all the valuable help which in many ways you gave me (*41*).

Roscoe's textbooks of chemistry were unusually successful, passed through edition after edition, and were translated into Russian, Italian, Hungarian, Polish, Swedish, modern Greek, Japanese, Urdu, Icelandic, Bengali, Turkish, Malayalam, and Tamil. His autobiography (*42*) was written with great charm, and the "Treatise on Chemistry" by Roscoe and Schorlemmer is familiar to all chemists.

Sir Henry's last years were spent on his beautiful estate at Woodcote in southern England. Here Lady Roscoe took endless pleasure in the cultivation of flowers and flowering shrubs and in entertaining her husband's distinguished guests. "My father," said Miss Roscoe, "delighted to bring foreigners, and the more heterogeneous they were the more he was pleased. I remember one luncheon party of late years, consisting of a Chinaman, a Japanese, a Czech, a German, and our three selves, and the Occidentals were much the quietest of the party" (*43*).

After enjoying a serene old age, Sir Henry E. Roscoe died suddenly on December 18, 1915, during an attack of angina pectoris.

In 1927 J. W. Marden and M. N. Rich of the research staff of the Westinghouse Lamp Company obtained metallic vanadium 99.9% pure by heating a mixture of vanadic oxide, metallic calcium, and calcium chloride in an electric furnace for an hour at a temperature of about 1400° Fahrenheit. When the resulting mass was cooled and stirred into cold water, beads of pure metallic vanadium separated out (*35*).

The alloy ferrovanadium is used extensively in the steel industry. The presence of small amounts of vanadium profoundly alters the properties of steel, greatly increasing its toughness, elasticity, and tensile strength. Thus the metal that Sefström and Berzelius named for the ancient Swedish goddess of beauty has come to play an important utilitarian rôle in the construction of locomotive frames, driving axles, and large shaftings for electrical machinery.

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XII. THE CHEMICAL CONTRIBUTIONS OF CHARLES HATCHETT

Unlike most chemists Charles Hatchett spent all his life in luxurious surroundings. He was born on January 2, 1765,* the son of a famous coach-builder of Long Acre, London, who in 1771 built at Chelsea a mansion called "Belle Vue House" (*1*), (*2*), (*3*).

Most of his scientific research was done during the decade 1796 to 1806. His first paper in the *Philosophical Transactions* described his analysis of the Carinthian lead molybdate (*4*). "The celebrated Scheele," said he, "in 1778 read before the Academy of Sciences at Stockholm an essay in which he proved . . . that the mineral called *Molybdaena* was composed of sulfur and a peculiar metallic substance, which, like arsenic and tungsten, was liable by super-oxygenation to be converted into a metallic acid which in its properties differed from any other that had been previously discovered." Hatchett mentioned the confirmatory researches of B. Pelletier, P. J. Hjelm, and "Mr. Islmann" [J. C. Ilsemann], and added: "But the existence of this substance was known to be only in that mineral which Scheele had examined." This lead mineral from Carinthia had been described by the Abbé F. X. Wulfen and by N. J. Jacquin. For several years it was believed to be lead tungstate, but Klaproth proved it to be lead molybdate. Since Klaproth had had an insufficient amount of the mineral, Hatchett made a complete analysis of it and investigated the properties of molybdic acid.

In the following year Hatchett was made a Fellow of the Royal Society. In 1798 he analyzed "an earthy substance," *sydneia*, which Josiah Wedgwood had found in New South Wales and another specimen of it provided by Sir Joseph Banks (*5*). This, according to Wedgwood, was composed of "a fine white sand, a soft white earth, some colourless micaceous particles, and some which were black." Hatchett found it to consist "of siliceous earth, alumine, oxide of iron, and black lead or graphite" and concluded "that the Sydneian genus, in future, must be omitted in the mineral system."

In the same year, he analyzed the water of the Mere of Diss (*6*). Benjamin Wiseman of Diss, Norfolk, had noticed that flint stones, calcareous spar, slate, and pottery left in this water from the summer of 1792 to August, 1795, acquired a metallic stain. He sent some of the water and some of the coated objects to the President and Council of the Royal Society, who forwarded them to Charles Hatchett for analysis. Although the deposit contained pyrite, the water, according to Hatchett, did "not

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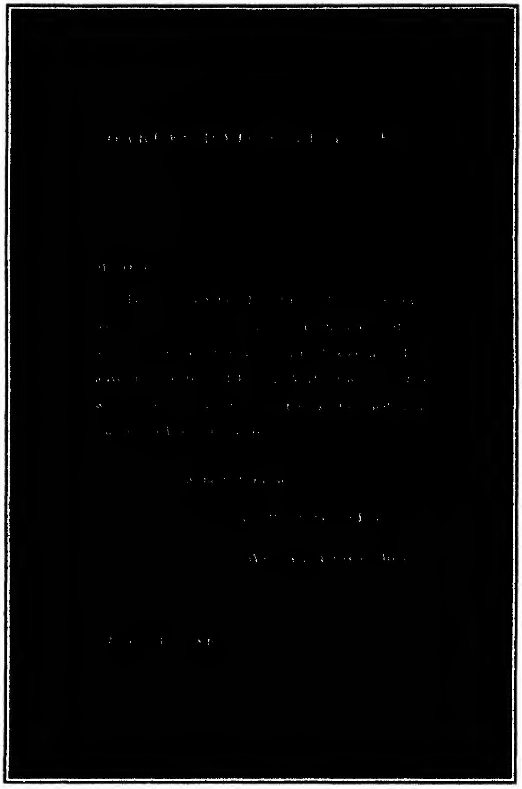
*** Most authors state that Hatchett was born "in about 1765." The 1935 "Annuaire" of the Académie des Sciences, however, in its list of members and correspondents, gives the definite date, January 2, 1765. This annual gives the date of his death as March 10, 1847, instead of February 10.**

hold in solution any sulphur and scarcely any iron; it has not therefore been concerned in forming the pyrites, but it appears to me that the pyritical matter is formed in the mud and filth of the Mere; for Mr. Wiseman says . . . that 'the Mere has received the silt of the streets for ages.' Now . . . sulphur is continually formed, or rather liberated, from putrefying animal and vegetable matter, . . . and this most probably has been the case at Diss. . ."



Courtesy Franklin Institute

Dedication page from Brande's "Manual of Chemistry," Third Edition, London, 1830.

In the following year Sir Everard Home interested Mr. Hatchett in the chemical composition of dental enamel (*7*), (*8*). Since the tooth of the elephant is composed of three different structures, Sir Everard wished to know "whether the materials themselves were different or only differently arranged." Hatchett showed that the enamel was composed of calcium phosphate. "The enamel," said he, "has been supposed not a phosphate but a carbonate of lime. This error may have arisen from its solubility in acetous acid or distilled vinegar; but the effects of the acetous acid are in every respect the same on powdered bone as on the enamel" (*8*).

Hatchett then investigated the composition of shell and bone. "When it is applied to the cuttle-bone of the shops. . .," said he, "the term bone is here misapplied. . . for this substance in composition is exactly similar to shell, and consists of various membranes hardened by carbonate of lime, without the smallest mixture of phosphate" (*8*).

Mr. Hatchett observed that the external skeleton of crustaceans and the egg shells of birds contain more calcium carbonate than calcium phosphate but that in bones the phosphate predominates. "It is possible," said he, ". . . that some bones may be found composed only of phosphate of lime:

and that thus shells containing only carbonate of lime and bones containing only phosphate of lime will form the two extremities in the chain. . ."

In 1800 he published a paper which won the approbation and interest of Sir Humphry Davy (*9*), (*10*). "Mr. Hatchett," said he, "has noticed in his excellent paper on zoöphytes that isinglass is almost wholly composed of gelatine. I have found that 100 grains of good and dry isinglass contain more than 98 grains of matter soluble in water . . ." Dr. John Bostock (1774–1846) also praised this paper. "The term mucus," said he, "had been generally employed in a vague and unrestricted sense until Mr. Hatchett . . . attempted to assign to it a more appropriate and definite meaning. He conceives that jelly and mucus are only modifications of the same substance . . . he considers it to be entitled to the appellation of mucus when it is soluble in cold water and cannot be brought to a gelatinous state . . . the ideas which I have formed of the nature of jelly and mucus . . . differ materially from those of Mr. Hatchett . . . Mr. Hatchett . . . speaks of the white of the egg as consisting of pure albumen, but I believe that in this particular he will be found not perfectly accurate. . ." Dr. Bostock had found it to contain also a small amount of a substance incapable of coagulation (*11*).

WILLIAM THOMAS BRANDE
1788–1866

British chemist and mineralogist. Successor to Sir Humphry Davy at the Royal Institution. Son-in-law of Charles Hatchett. Author of Brande's "Manual of Chemistry." Lecturer on mineralogical chemistry.

Soon after the turn of the century, Mr. Hatchett became interested in William Thomas Brande, a young apothecaries' apprentice who had recently moved to Chiswick. He encouraged the boy to collect and classify ores and rocks, and presented him with some of his duplicate specimens; the boy, in turn, sometimes assisted Mr. Hatchett in analyzing minerals (*1*). Brande's first scientific paper was published in *Nicholson's Journal* when he was only sixteen years old. When he became Sir Humphry Davy's successor at the Royal Institution, Brande increased the mineral collection and used it in his lectures. He later married Charles Hatchett's daughter.

Hatchett's greatest achievement was probably his discovery of the metal columbium (*12*). While he was arranging some minerals at the British

Museum, one of them attracted his attention. From Sir Hans Sloane's catalogue he found that it had been sent by "Mr. Winthrop of Massachusetts."

Early accounts of the discovery of columbite differ in several important respects. While examining some minerals in the British Museum, half a century after the death of its founder, Sir Hans Sloane, Charles Hatchett became interested in a small, dark, heavy specimen which bore some resemblance to the "Siberian chromate of iron" on which he was then making some experiments.

"Upon referring to Sir Hans Sloane's catalogue," said Hatchett before the Royal Society on November 26, 1801, "I found that this specimen was only described as 'a very heavy black stone, with golden streaks' which proved to be yellow mica; and it appeared that it had been sent with various specimens of iron ores to Sir Hans Sloane by Mr. Winthrop of Massachusetts. The name of the mine, or place where it was found, is also noted in the catalogue; the writing, however, is scarcely legible: it appears to be an Indian name (Nautneague); but I am informed by several American gentlemen that many of the Indian names (by which certain small districts, hills, etc., were forty or fifty years ago distinguished) are now totally forgotten, and European names have been adopted in the room of them. This may have been the case in the present instance; but, as the other specimens sent by Mr. Winthrop were from the mines of Massachusetts, there is every reason to believe that the mineral substance in question came from one of them, although it may not now be easy to identify the particular mine" (*12*).

Printed by C. Hullmandel
From T. Faulkner's "Historical and topographical description of Chelsea" 1829

SIR HANS SLOANE
1660–1753

British physician and collector. Editor of the *Philosophical Transactions.* President of the Royal Society. The books, pictures, coins, and specimens which he bequeathed to the nation became the nucleus of the British Museum. The specimen of columbite in which Hatchett discovered columbium was from this collection.

In the following January, *Nicholson's Journal* stated that "the mineral was sent with some iron ores to Sir Hans Sloane by Mr. Winthrop of Massachusetts [sic], and there is therefore every reason to believe that it came from some of the iron mines in that province [sic]" (*12*).

In the fall of the same year, the *Medical Repository* made a preliminary announcement of Hatchett's discovery of "a metal in an ore lately brought from North-America . . . . We have no particular information from what spot or region the mineral was procured" (*36*).

After reading Hatchett's paper in the *Philosophical Transactions* (*12*), Samuel Latham Mitchill, editor, published an abstract of it in his *Medical Repository* (*36*). In commenting on the name "Nautneague" he said, "From the same place, it is probable, more of the like ore can be obtained. This is particularly desirable, as Mr. Hatchett has had so small a piece to work upon, and no other specimen but the half which he reserved for the museum is known to exist. We hope the gentlemen of Massachusetts, who respect Mr. Winthrop's memory and are acquainted with the scope and direction of his researches, will find out the mine and procure more samples of this singular mineral. We think this matter would not be unworthy of that excellent institution the Historical Society" (*36*).

"No complete disoxydation of it," continued Mitchill, "has as yet been effected. The pure metal, therefore, has not been seen, even by Mr. Hatchett himself. And if this discerning experimenter had succeeded in freeing the metal from its oxygen, the quantity he worked upon was so very small that it would have been impossible to have gratified many of the curious by presents. At this time it is not known what quantity may exist in nature, nor to what economical uses it may be applied.

"While we express our hopes that the whole history of this Columbian mineral will soon be made known, we sincerely deplore the afflicting and untimely death of our friend and countryman, Mr. Thomas P. Smith, from whose industry, acuteness, and zeal in chemical (and, indeed, almost the whole circle of physical) researches, Mr. Hatchett informs the Royal Society he had anticipated important aid in this inquiry" (*36*).

In his annual oration before the Chemical Society of Philadelphia in 1798, this youthful chemist voiced his conviction that "The only true bases on which the *Independence* of our country can rest are *Agriculture* and *Manufactures*. To the promotion of these nothing tends in a higher degree than Chemistry . . . . It is to a general diffusion of a knowledge of this science, next to the *Virtue* of our countrymen, that we are to look for the firm establishment of our *Independence*" (*47*). In the return journey from England, Thomas P. Smith died "in consequence of the bursting of a gun" at the age of only twenty-five years (*36*). Mrs. Gertrude D. Hess, assistant librarian, kindly searched the manuscripts of the American Philosophical Society by and pertaining to Thomas P. Smith, but was unable to find there any mention of columbite.

In the spring of 1805 the *Medical Repository* published an article entitled "Place where the ore of columbium was found" (*37*). "It has been ascertained," the article stated, "that the specimen of this metal [sic] upon which the experiments were made, as mentioned in our *Med. Rep. Hex. i*, vol. vi., p. 322, was taken from a spring of water in the town of New London, in the State of Connecticut. The fountain is near the house in which Governor Winthrop used to live, and is about three miles distant from the margin of salt water, at the head of the harbour. This is the spot heretofore called Nautneague; which is in Connecticut and not in Massachusetts. By the politeness of Francis B. Winthrop, Esq., of New York, the manuscript papers of his ancestor, relative to this place and to the minerals he carried to Hans Sloane, have been sent to the Historical Society of Massachusetts. By their care, we hope, every interesting particular concerning this substance and the place where it was orginally found will be made known to the public. It will then be easy for gentlemen to visit the spot and to collect other specimens of this singular ore" (*37*).

In the same year A.-L. Millin published in his *Magasin Encyclopédique* what seems to be a rather inaccurate French translation of the preceding article. He said he had obtained the information from M. Valentin, a physician and skilful physicist and naturalist of Marseilles (*38*).

The "Mr. Winthrop of Massachusetts" referred to by Charles Hatchett was John Winthrop (1681–1747), grandson of the first governor of Connecticut and great grandson of the first governor of Massachusetts. He was a Fellow and very active member of the Royal Society. Like his paternal grandfather, who had been one of the original Fellows of this Society, he liked to collect natural objects. The Journal Book of the Royal Society for June 27, 1734, stated that "Mr. Winthrop presented several curiosities from New England, as contained in the following list.... These curiosities are a part of a large collection shewn at several meetings during the subsequent winter, and the whole catalogue to which these numbers refer is entered after the minutes of the day" (*39*). Sir Hans Sloane was then President of the Royal Society (*40*).

In 1844 Benjamin Silliman and Benjamin Silliman, Jr., published this historic list in their *American Journal of Science* and remarked in a footnote that "it has been supposed that the original specimen on which Mr. Hatchett made the discovery of *columbic acid* was sent in this invoice, and that some hint as to the locality from whence it came might be had" (*39*). The only entry the Sillimans could find in this list, however, that corresponded at all with Hatchett's description of columbite was "No. 348. A black mineral, very heavy, from the inland parts of the country." They concluded that "we must therefore rest content probably in ignorance of the exact locality of that interesting specimen, although mineralogists have, on what evidence does not appear, considered New London as the locality" (*39*).

Berzelius even doubted the American origin of columbite. In a letter to Thomas Thomson in the autumn of 1814 (see page 191), he stated that "Mr. Hatchett gave this name after the place where it was thought the fossil had been found; now it is not good practice to name elementary substances in chemistry after the places where they have first been found; not to mention the fact that the place where columbite was found is still doubtful, in the same degree as it is not certain that it comes from America."

In his *Report on the Geological Survey of the State of Connecticut,* Dr. Charles Upham Shepard said of columbite: "The State of Connecticut furnished the first sample of this ore to science .... The chinastone quarry at Middletown has furnished the most extraordinary specimens of columbite yet described in the world. A single group of crystals obtained at this place weighed fourteen pounds .... It is also found in small quantity at Haddam .... The first sample was sent by Governor Winthrop to Sir Hans Sloane, and was deposited with the collection of the gentleman in the British Museum, where it was examined by Mr. Hatchett, and afterwards by Dr. Wollaston. The specimen was supposed to have been found near New London, which was the residence of Governor Winthrop; but as the ore has not been rediscovered in that vicinity, it is more probable that it was obtained from the region of Middletown" (*41*).

Since Sir Hans Sloane was only sixteen years old when Governor Winthrop died, Shepard's statement that the columbite had been sent to Sloane by Governor Winthrop is probably erroneous. Hatchett's remark in 1801 that many Indian names (such as Nautneague) which were used "forty or fifty years ago . . . are now totally forgotten" implies that he understood that the original specimen of columbite must have been labeled in about the middle of the eighteenth century (*12*). He referred to the sender, moreover, not as "Governor" Winthrop but as "Mr." Winthrop.

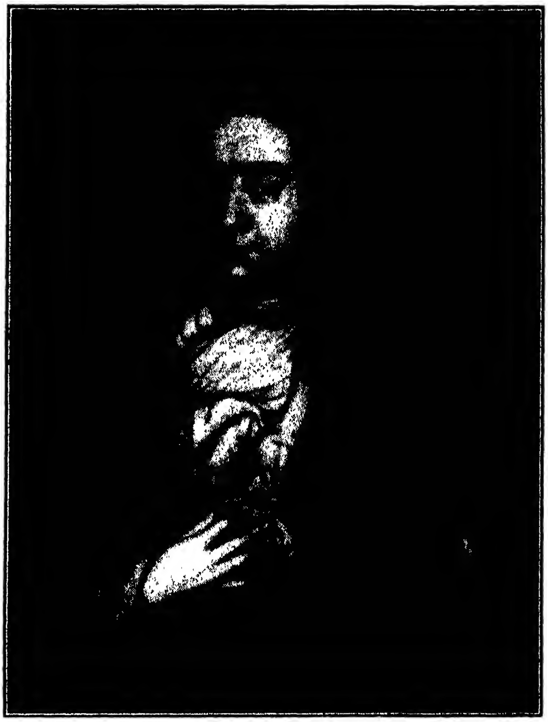
In his "Chemistry in Old Philadelphia" Edgar F. Smith stated that "Hatchett found . . . a new element in a mineral of the Royal Society Collection which had been sent in from Haddam, Connecticut, and been called there *columbite* by Governor Winthrop" (*42*).

In an article on the life and mineral collection of Sir Hans Sloane, Jessie M. Sweet states that "The only specimen which fortunately is still in the Mineral Collection is the original fragment of columbite (B. M. 60309), of which a brief account may be given here. Sloane describes it in the catalogue of "Metalls," No. 2029, as: A very heavy black stone with golden streaks . . . from Nautneague. From Mr. Winthrop" (*40*).

Miss Sweet adds that when John Winthrop (1681–1747) was elected a Fellow of the Royal Society in 1734, "he presented more than six hundred specimens (mostly minerals), together with a manuscript catalogue of them to the Society . . . . Many of these specimens appear to have been incorporated into the Sloane collection, as several entries in the Winthrop and Sloane manuscript catalogues are identical, and the columbite probably came from Winthrop at that time" (*40*).

Miss Sweet also stated that "it was surmised that 'Nautneague' was another name for Naumeaug (now New London, Connecticut), and the specimen was believed to have been found in a spring of water, near the house of Governor Winthrop . . . . The columbite is figured and described in James Sowerby's Exotic Mineralogy, 1811–1820, vol. 1, p. 11 and plate 6, and compares favourably with Sloane's description, but now the specimen has no longer any 'golden streaks'" (*40*).

In 1940 Dr. C. A. Browne wrote Mr. Allyn B. Forbes of the Massachusetts Historical Society for information regarding the manuscript paper which Francis B. Winthrop of New York is said to have sent to this Society. According to *Nicholson's Journal* for 1806, this manuscript referred to the mineral which F. B. Winthrop's "ancestor" had given Sir Hans Sloane and to the place where it was found (*43*). However, no trace of such a document could be found. Francis B. Winthrop (1754–1817) was a grandson of John Winthrop (1681–1747) and great-great-grandson of the first governor of Connecticut (*44*).

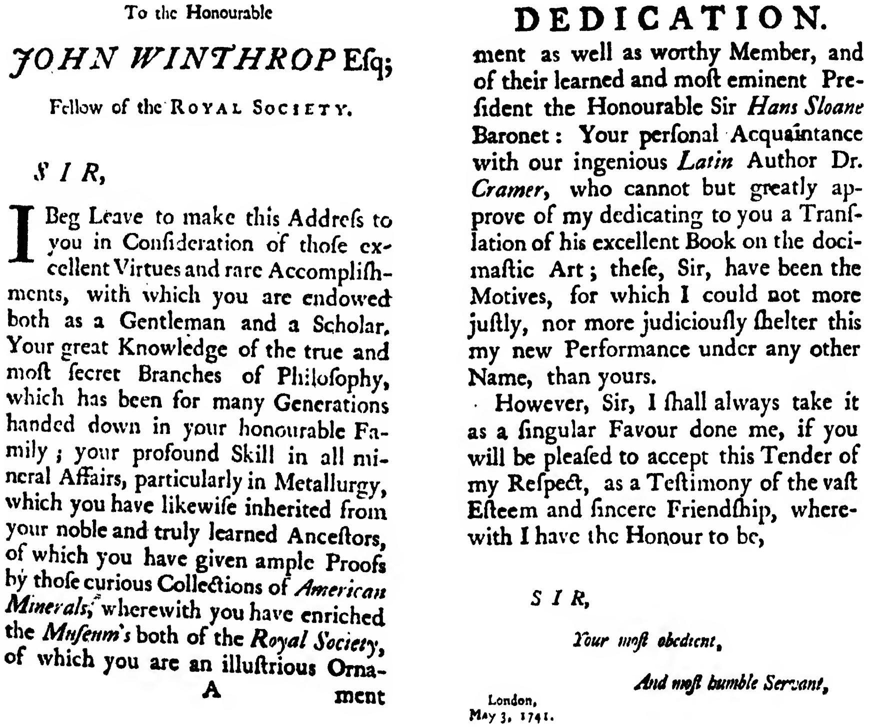


Courtesy Massachusetts Historical Society

JOHN WINTHROP
1681–1747

The specimen of columbite which Hatchett analyzed had been sent to the Royal Society by this John Winthrop, a grandson of John Winthrop, first governor of Connecticut. This portrait was reproduced from a copy in the collections of the Massachusetts Historical Society. Volume 40 (1737–38) of the *Philosophical Transactions* was dedicated to him by Cromwell Mortimer, Secretary of the Royal Society.

The Massachusetts Historical Society has preserved a commonplace book which originally belonged to John Winthrop (1681–1747). In it there is a letter which Francis B. Winthrop wrote to his brother Thomas L. Winthrop of Boston on September 10, 1803, describing the spring at New London in connection with their grandfather. "I think you must remember this spring," said he, "It is about three miles from the sea, which answers to the distance in the memo of articles presented to the Royal Society" (*45*).



To the Honourable

JOHN WINTHROP Eſq;

Fellow of the ROYAL SOCIETY.

SIR,

I Beg Leave to make this Addreſs to you in Conſideration of thoſe excellent Virtues and rare Accompliſhments, with which you are endowed both as a Gentleman and a Scholar. Your great Knowledge of the true and moſt ſecret Branches of Philoſophy, which has been for many Generations handed down in your honourable Family; your profound Skill in all mineral Affairs, particularly in Metallurgy, which you have likewiſe inherited from your noble and truly learned Anceſtors, of which you have given ample Proofs by thoſe curious Collections of *American Minerals*, wherewith you have enriched the *Muſeum's* both of the *Royal Society*, of which you are an illuſtrious Ornament as well as worthy Member, and of their learned and moſt eminent Preſident the Honourable Sir *Hans Sloane* Baronet: Your perſonal Acquaintance with our ingenious *Latin* Author Dr. *Cramer*, who cannot but greatly approve of my dedicating to you a Tranſlation of his excellent Book on the docimaſtic Art; theſe, Sir, have been the Motives, for which I could not more juſtly, nor more judiciouſly ſhelter this my new Performance under any other Name, than yours.

However, Sir, I ſhall always take it as a ſingular Favour done me, if you will be pleaſed to accept this Tender of my Reſpect, as a Teſtimony of the vaſt Eſteem and ſincere Friendſhip, wherewith I have the Honour to be,

SIR,

Your moſt obedient,

And moſt humble Servant,

London,
May 3, 1741.

Dedication of the English translation of J. A. Cramer's "Elements of the Art of Assaying Metals," London, 1741. It refers to John Winthrop (1681-1747), grandson of the first governor of Connecticut.

In the letters of Governor John Winthrop the Younger, published with the Winthrop Papers of the Massachusetts Historical Collections, there is no mention of columbite. His interest in minerals, despite the difficulty of collecting them, is expressed, however, in a letter to Sir Robert Moray on August 18, 1668. "I have been very inquisitive," wrote the Governor, "after all sorts of mineralls, w^{ch} this wildernesse may probably affoard; but indeed the constant warrs, w^{ch} have continued amongst the Indians since I came last over, hath hindred all progresse in searching out such matters . . . . Those shewes of minerals, w^{ch} we have frō the Indians doe only demonstrate that such are in reality in the country, but they usually bring but small pieces, w^{ch} are found accidentally in their huntings, sticking in some rock or on the surface of the earth, on the side of some hill, or banke of a river . . ." (*46*).

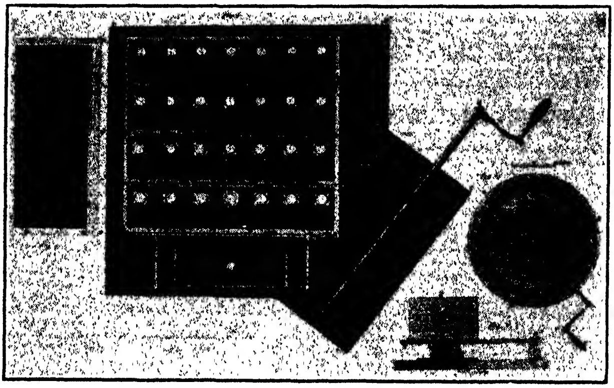
From the existing evidence, it seems impossible to prove conclusively whether columbite was discovered by John Winthrop the Younger, first governor of Connecticut, and bequeathed to his grandson, John Winthrop (1681–1747), or whether it was originally discovered by the grandson. It is possible, however, that this question may some day be settled by the finding of hitherto unknown documents.

Hatchett fused the ore with potassium carbonate. When he took up the melt with boiling water, a brown residue remained. When nitric acid was added to the yellow filtrate, a copious white precipitate was thrown down. "The preceding experiments shew," said he, "that the ore which has been analyzed consists of iron combined with an unknown substance and that the latter constitutes more than three fourths of the whole. This substance is proved to be of a metallic nature by the coloured precipitates which it forms with prussiate of potash and with tincture of galls; by the effects which zinc produces when immersed in the acid solutions; and by the colour which it communicates . . . to concrete phosphoric acid, when melted with it. . ." He mentioned that it retained oxygen tenaciously and that the oxide was acidic. Although the specimen Hatchett analyzed was very small, he hoped to get more soon from "a gentleman now in England (Mr. Smith, Secretary to the American Philosophical Society)." This was evidently Thomas P. Smith, who died in 1802. In his "Chemistry in America," Dr. Edgar Fahs Smith quotes from the *National Intelligencer*, "While we express our hopes that the whole history of this Columbian mineral will soon be made known, we sincerely deplore the afflicting and untimely death of our friend and countryman, Mr. Thomas P. Smith, from whose industry, acuteness and zeal in chemical . . . researches, Mr. Hatchett informs the Royal Society he had anticipated important aid in this inquiry."

Hatchett named the new metal *columbium* and stated that its "olive green prussiate and the orange-coloured gallate . . . may probably be employed with advantage as pigments." He also described his unsuccessful attempts to reduce the oxide to the metal. From his careful use of Lavoisier's new nomenclature, it is evident that Hatchett was not a phlogistonist.

In 1798 the Committee of Privy Council for considering the state of the coinage reported that the gold coin was suffering considerable losses in weight, and requested Henry Cavendish and Charles Hatchett to examine it "to ascertain whether this loss was occasioned by any defect" (*13*). Their experiments were begun near the end of 1798 and completed in April, 1801. At Cavendish's request the report was made by Hatchett alone. Hatchett stated, however, "... At all times I was favoured with his valuable advice; and the machines to produce friction, as well as the dies were entirely contrived by himself. . ."

Hatchett studied the binary alloys of gold with arsenic, antimony, zinc, cobalt, nickel, manganese, bismuth, lead, tin, iron, platinum, copper, and silver, and confirmed the prevailing opinion that of these metals only copper and silver are suitable for alloying gold for coinage. He concluded "that gold made standard by silver and copper is rather to be preferred for coin. . ." and added that "there is commonly some silver in the gold which is sent to the Mint." He also stated, not without humor, that "our gold coin suffers but little by friction against itself; and the chief cause of natural and fair wear probably arises from extraneous and gritty particles; . . . the united effect of every species of friction to which they may be subjected, *fairly and unavoidably*, during circulation. . . will by no means account for the great and rapid diminution which has been observed in the gold coin of this country . . ." He added that the study of alloys had not kept pace with the rapid progress of chemistry and that "Few additions have been made to the compound metals employed by the ancients."



(Phil. Trans., 1803)

Apparatus designed by Henry Cavendish and used by Charles Hatchett for determining the comparative wear of gold when alloyed by various metals. Two frames, one above the other, each carrying twenty-eight coins, rubbed the upper coins backward and forward over the ones below. Each of the smaller concentric circles represents a coin. To avoid the formation of furrows, the direction in which the coins rubbed against each other was made to vary continually.

In 1804 he published an analysis of a "triple sulphuret of lead, antimony, and copper." James Smithson (1765–1829), founder of the Smithsonian Institution, disagreed with his conclusions. "It is not probable," said he, "that the present ore is a direct quadruple combination of the three metals and sulphur and that these, in their simple states, are its immediate component parts; it is much more credible that it is a combination of the three sulphurets of these metals. . ." (*14*), (*15*).

At the same time Hatchett became interested in lac (*16*). Geoffroy the Younger and J. A. C. Chaptal had regarded it as a kind of wax, but F. C. Gren and A.-F. Fourcroy believed it to be a true resin. Hatchett concluded "that although lac is indisputably the production of insects, yet . . . the greater part of its aggregate properties, as well as of its component ingredients, are such as more immediately appertain to vegetable bodies . . ."

In 1804 he analyzed a strongly magnetic specimen of pyrite (*17*) to determine whether the magnetic polarity was inherent in the iron sulfide or whether minute particles of "the ordinary magnetical iron ore" [magnetite] were interspersed in it. Although he could find no previous mention of magnetic iron sulfide, Hatchett proved experimentally "that the three inflammable substances, carbon, sulphur, and phosphorus . . . possess the property of enabling iron to retain the power of magnetism . . ."

He continued the study of bitumens which he had begun in 1798 and strengthened the evidence "that bituminous substances are derived from the organized kingdoms of nature, and especially from vegetable bodies." He analyzed a "schistus" (*18*) which Sir Joseph Banks had found near a geyser near Reykum, Iceland, and found it to consist of water, oily bitumen, mixed gas, charcoal, silica, oxide of iron, and alumina.

When Sir James Hall (1761–1832) read of this work, he recalled his own experiments on "the effects of compression in modifying the effects of heat," and concluded that "the changes which, with true scientific modesty, he [Hatchett] ascribes to an unknown cause, may have resulted from various heats acting under pressure of various force" (*19*). Sir James subjected the theories of the geologists to the test of chemical experiment and showed that when limestone is heated under pressure, it is not converted into quicklime but into crystalline marble.

After analyzing some specimens from a pitch lake of Trinidad, Hatchett concluded that "a considerable part of the aggregate mass at Trinidad was not pure mineral pitch or asphaltum, but rather a porous stone of the argillaceous genus, much impregnated with bitumen. The specimens he analyzed, however, were not representative of the lake as a whole" (*20*).

In 1804 William Nicholson, the editor, chose Mr. Hatchett and Edward Howard to serve with him on a committee to judge Richard Chenevix's alloy of platinum and mercury which Chenevix believed identical with palladium, the new metal which had been announced anonymously by W. H. Wollaston. Hatchett saw with his own eyes some of the experiments made by the enthusiastic but misguided Chenevix.

During the years 1805 and 1806 Hatchett published three papers on an artificial tanning agent (*21*). He mentioned the researches of Nicolas

Deyeux (1745–1837), Armand Seguin (1767–1835), and Sir Humphry Davy on the natural tanning agents, and added that R. Chenevix had "observed that a decoction of coffee-berries did not precipitate gelatine unless they had been previously roasted; so that tannin had in this case either been formed or had been developed from the other vegetable principles by the effects of heat."

Revue Illustrée, 1886
Sketch by P Renouard.

MICHEL-EUGÈNE CHEVREUL
1786–1889

French chemist and psychologist who made notable contributions to the chemistry of fats and oils, soap, candles, and dyes. He lived to be almost one hundred and three years old, sound and active in mind and body. This sketch was made at his centenary, a gala occasion in Paris. When he investigated Hatchett's artificial tanning agents, Chevreul was only twenty-four years old (twenty-one years younger than Hatchett). See ref. (*48*).

Hatchett treated various kinds of wood, coal, and coke with nitric acid and found that "a substance very analogous to tannin . . . may at any time be produced by exposing carbonaceous substances, whether vegetable, animal, or mineral, to the action of nitric acid." He also "converted skin into leather by means of materials which, to professional men, must appear extraordinary, such as deal sawdust, asphaltum, common turpentine, pit coal, wax candle, and a piece of the same sort of skin . . ."

Dr. John Bostock tried unsuccessfully to use Hatchetts artificial tan as a test for "jelly" [gelatine]. Although it had been stated "on the highest authority, that of Mr. Hatchett and Mr. Davy . . . that isinglass consists of nearly pure jelly," Dr. Bostock found that isinglass from the shops contained a certain amount of insoluble matter which he believed to be coagulated albumen. Dr. G. Melandri of Milan also investigated Hatchett's tannin.

M.-E. Chevreul, near the beginning of his surprisingly long career, studied Hatchett's papers and prepared some of the "tannin." Hatchett had found that pit-coal which contained no resinous substance was dissolved completely by nitric acid and converted into the artificial tannin, whereas any resinous matter remained undissolved. When Chevreul treated pit-coal with nitric acid, however, evaporated the solution, and poured it into water, "a yellow matter separated, which was much more abundant than what remained in solution, and had no property that rendered it similar to resins . . . yet I do not allow myself," said Chevreul, "the least reflection on the labours of that celebrated English chemist, as I am too fully aware that different modes of operating and the different varieties of the bodies examined . . . may produce a variation in the results . . ." Chevreul found that the water-soluble substance which precipitated gelatine copiously was a compound of nitric acid and carbonaceous matter . . ." (*22*). These artificial tannins have since been identified as picric acid and other nitro derivatives of phenols (*23*).

Thomas Thomson said in 1810, "Till lately the analysis of vegetable substances was almost entirely overlooked by British chemists; but the fineness of the field has now begun to attract their attention. Experiments of great importance have been published by Davy, Chenevix &c and above all by Hatchett . . ." (*24*).

On February 21, 1809, Hatchett became a member of the famous Literary Club which had been founded in 1764 by Dr. Samuel Johnson and Sir Joshua Reynolds. As treasurer of the club, Hatchett prepared a brief historical account of it, which appears in Boswell's "Life of Johnson" (*25*). The club also included, among others, Edmund Burke, Oliver Goldsmith, David Garrick, Edward Gibbon, Adam Smith, Sir Joseph Banks, Sir Charles Blagden, Sir Humphry Davy, Dr. W. H. Wollaston, Sir Walter Scott, Sir Thomas Lawrence, and Dr. Thomas Young.

Hatchett also took an active part in the *Animal Chemistry Club*, which met alternately at his home and that of Sir Everard Home. Once every three months, Sir Benjamin Brodie, Sir Humphry Davy, W. T. Brande, Mr. John George Children, and a few others dined with the two hosts and discussed their researches in physiological chemistry (*26*), (*27*), (*28*). According to Sir Benjamin Brodie, "they were very rational meetings, in which a good deal of scientific discussion was mixed up with lively and agreeable conversation. The society continued to exist for ten or eleven years, but during the latter part of the time, some other members were added to it, and it degenerated into a mere dinner club . . . Hatchett, who had now inherited a considerable fortune on the death of his father, had ceased to work in chemistry (in spite of the remonstrance of Sir Joseph Banks, who used to say to him in his rough way that 'he would find being a gentleman of fortune was a confounded bad trade'), but he had previously laid up a large store of knowledge, abounded in the materials of conversation, and was a delightful companion . . ." (*28*).

Hatchett was one of the "educated men, with the sagacity for which this nation is famous" who helped to entertain Berzelius in 1812 (*29*). Since Berzelius understood little of what the English chemists were saying, he had a dull time at Hatchett's dinner party. It was there, nevertheless, that he first made the acquaintance of Dr. Alexander Marcet.

In his travel diary Berzelius wrote, "Hatchett himself is a very agreeable man of about forty to forty-five years. His father was a rich coach-maker, and the son, although a famous chemist at the time of his father's death, has continued to carry on the business. He is in very good circumstances, and lives in Roehampton on a little estate built in a fine Italian style and excellently maintained . . . Close by his Italian villa he has a very well-equipped laboratory, but for a long time he has not worked" (*30*).

When the English translation of Berzelius' treatise on the composition of animal fluids appeared, Dr. Marcet wrote, "Your great memoir is an honour to us. Hatchett, however, complains that, when you hunted in his grounds, you didn't even cite him; but I have explained to him, as best I could, the haste in which you found yourself and your necessity of abstaining from reference work."

"I am very sorry," replied Berzelius, ". . . . but if you take this matter up with him again, tell him that I am absolutely ignorant of any work of his on these subjects other than that of the testaceae. . ." Berzelius also explained that he had confined himself almost entirely to a description of his own work. Dr. Marcet replied, "I gave your little compliment to Hatchett, who seemed entirely satisfied with it, and sends you his best regards. You will see on consulting *Thomson* [Thomas Thomson, "A system of chemistry," 1810] that he has written more than once on animal substances" (*29*).

CHARLES HATCHETT

This portrait was lithographed by Day and Haghe from the painting by Thomas Phillips, and published in 1836 by Thomas McLean.

In 1813 Hatchett published in the *Annals of Philosophy* a method of separating iron and manganese (*31*). This paper was in the form of a letter to Thomas Thomson, the editor, and was dated "Mount Clare, Roehampton, Sept. 25, 1813." A. F. Gehlen had used succinic acid to separate these two metals, Professor J. F. John had used oxalic acid, but Hatchett simply precipitated the ferric hydroxide from a neutral solution containing ammonium chloride, leaving the manganese in solution.

In 1817 he described a method of renovating musty "corn" [wheat] by floating off the damaged grain with boiling water and carefully drying the rest (*32*).

In his history of Chelsea (*33*), Thomas Faulkner has left a contemporary description of Hatchett's fine home, Belle Vue House. "This capital mansion," says Faulkner, "was built by Mr. Hatchett's father in 1771; and the weeping willow opposite to the house, reckoned one of the finest trees of its kind in England, was planted by him in 1776; it commands beautiful views of the Thames and the distant Surrey Hills." In the house were paintings by several great masters, a portrait of Mrs. Hatchett by Gainsborough, a large organ, a collection of manuscript and printed music, and some Mongol idols collected by Hatchett's friend Peter Simon Pallas, the famous traveler. "The Library," said Faulkner, "is extensive, and contains many valuable editions of the Greek and Latin Classics, together with a numerous series of Historical Works, and the voluminous Transactions and Memoirs of the Royal Society and other similar learned Institutions of Europe."

In December, 1818, Dr. Marcet wrote to Berzelius, "Wollaston, [Sir William] Congreve, and Hatchett are hard at work, but up to the present haven't produced anything." Three years later he wrote: "Hatchett is taking care of his money and paying court to personages with grand titles; but is no longer doing anything in chemistry, and I do not even know that he is showing much interest in what others are doing" (*29*). He must have retained some interest, however, for on September 15, 1823, he was elected as a correspondent for the chemical section of the *Académie des Sciences*. In 1836 Hatchett published a quarto brochure on "The spikenard of the ancients." He died at his home, Belle Vue House, Chelsea, on February 10, 1847, at the age of eighty-two years.

In 1821 the Reverend J. J. Conybeare (1779–1824) named an Australian mineral in honor of "the eminent chemist to whom we are indebted for the most valuable contributions towards the history and analysis of this class of mineral substances"; this form of mineral tallow is still known as *hatchettine* or *hatchettite*. He found later, however, that it was identical with the substance W. T. Brande had referred to as *mineral adipocere* (*34*).

In 1877 the American mineralogical chemist J. Lawrence Smith named a mineral from North Carolina, a columbate of uranium, *hatchettolite*, because Hatchett's discovery of columbium "was clear, precise, and well made out, and has never been controverted" (*35*).

The author wishes to thank Dr. C. A. Browne and Mr. Allyn B. Forbes for kindly placing at her disposal their correspondence on the history of columbite, and Mrs. Gertrude D. Hess for examining the papers which Thomas P. Smith bequeathed to the American Philosophical Society.

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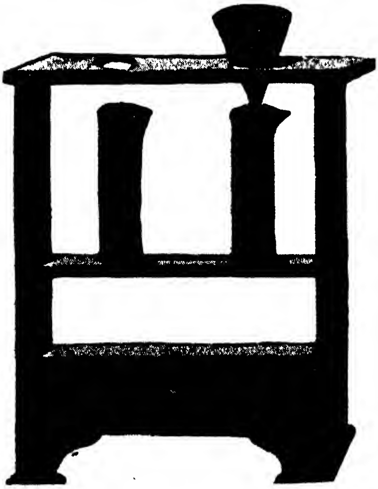

XIII. THE SCIENTIFIC CONTRIBUTIONS OF DON ANDRÉS MANUEL DEL RÍO*

Although A. M. del Río, the eminent discoverer of the element now known as vanadium, spent most of his active life in Mexico and a few years in Philadelphia, his services to chemistry and mineralogy are not as widely known and appreciated by American scientists as they deserve to be. He was a schoolmate and honored friend of Baron Alexander von Humboldt and a worthy colleague of Don Fausto de Elhuyar, first director of the School of Mines of Mexico.

. . . . . .

Andrés Manuel del Río y Fernández was born on Ave Maria Street in Madrid on November 10, 1764,† and received his preliminary training at the College of San Isidro. At the age of fifteen years he completed his courses in Latin, Greek, literature, and theology and received his Bachelor's degree from the famous University of Alcalá de Henares, which, two centuries before, had rivaled Salamanca. When Don José Solano held a public contest in experimental physics, the young graduate in theology distinguished himself so highly that the King provided for his further education at the Mining Academy of Almadén. Because of del Río's enthusiasm for mining and subterranean geometry, the Minister of the Indies, Don Diego Gardoqui, selected him to study in France, England, and Germany at government expense (*1*).

He studied chemistry in Paris under Jean Darcet and attended lectures in medicine and natural history. In 1789 he enrolled at the Royal School of Mines in Freiberg, Saxony, where great things were expected of him because of the enviable records made previously by his fellow countrymen Don Juan José and Don Fausto de Elhuyar. He, too, soon felt the charm of A. G. Werner's teaching of geognosy and mineralogy. One of del Río's intimate friends at the Freiberg Academy was his schoolmate, Baron Alexander von Humboldt, who later renewed the friendship in Mexico. Del Río also studied subterranean geometry, analytical chemistry, and metallurgy at the Royal School of Mining and Forestry at Schemnitz, Hungary (Štiávnica Baňská, Czechoslovakia).

In 1791 Señor del Río visited the metallurgical industries of England. During a second sojourn in France, he was associated with Lavoisier, and in the troublous days of 1793, he, too, almost fell prey to the fury of the revolutionists. According to Ramírez (*1*), del Río disguised himself as a water carrier and escaped to England. Although offered the directorships of several mining enterprises, he declined them.

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* **Presented before the Division of History of Chemistry at the Cleveland meeting of the A. C. S., Sept. 11, 1934.**

† **Although the year of del Río's birth has frequently been given as 1765, Ramírez (Ref. *1*) obtained the above date from the birth certificate.**

In 1793 a royal order decreed that Werner's theory of the formation of veins be taught at the School of Mines of Mexico recently founded by Don Fausto de Elhuyar (*2*). The professorship of mineralogy was therefore offered to Señor del Río, who had previously declined that of chemistry. Early in August, 1794, he set sail from Cadiz on the warship San Pedro Alcántara, taking with him a servant and a supply of apparatus for the School of Mines. Eleven weeks later he disembarked at Vera Cruz (*3*).

After arriving at Mexico City, del Río immediately arranged the mineral collections and planned his course in oryctognosy, which included mineralogy, geognosy, and paleontology and which began on April 27, 1795. The new world spread forth before him so many objects of scientific inquiry that he afterward wrote with enthusiasm: "Each step of the traveler in this Republic discovers to him something new" (*4*).

In 1795 he published the first edition of his "Elements of Oryctognosy" (*5*), which von Humboldt regarded as "the best mineralogical work which Spanish literature possesses" (*6*), and which Santiago Ramírez (*7*) called "a monumental work, which . . . will be an object of veneration and consultation by the mineralogists of our country and for all those who . . . are occupied in studying the mineralogy of our native country."

Del Río's paper on the best method of sinking mine shafts was printed for use in all the mines of Mexico, and his article on the relations between the composition of a mineral and the materials of which the vein is composed was published in the supplement to the *Gaceta de México* on January 18, 1797 (*1*), (*3*).

The most outstanding achievement of del Río's long, useful life was his discovery in 1801 of the metal now known as vanadium. He found that the brown lead mineral, *plomo pardo de Zimapán* (*8*), from the Cardonal Mine in Hidalgo contained what he believed to be a new metal. Because its salts are of varied colors, he at first called it *panchromium*, but because its salts with the alkalies and earths become red on heating or on treatment with acids, he later changed the name to *erythronium* (*1*), (*9*), (*10*).

When von Humboldt visited Mexico in 1803, del Río gave him several specimens of the brown lead ore. Von Humboldt sent some of them to the *Institut de France* with an explanatory letter giving del Río's analysis and his conclusions regarding the close resemblance of the new metal to chromium and uranium. A more detailed description addressed to Chaptal was lost in a shipwreck (*10*).

Since the properties of erythronium closely resembled those which Fourcroy had ascribed to the recently discovered metal chromium, del Río lost confidence in the importance of his discovery and concluded that his supposed new element was, after all, nothing but chromium (*11*). In a note to his translation of Karsten's "Mineralogical Tables" he wrote (*7*), (*9*), (*12*): ". . . but, knowing that chromium also gives by evaporation red or yellow salts, I believe that the brown lead is a yellow oxide of chromium, combined with excess lead also in form of the yellow oxide."

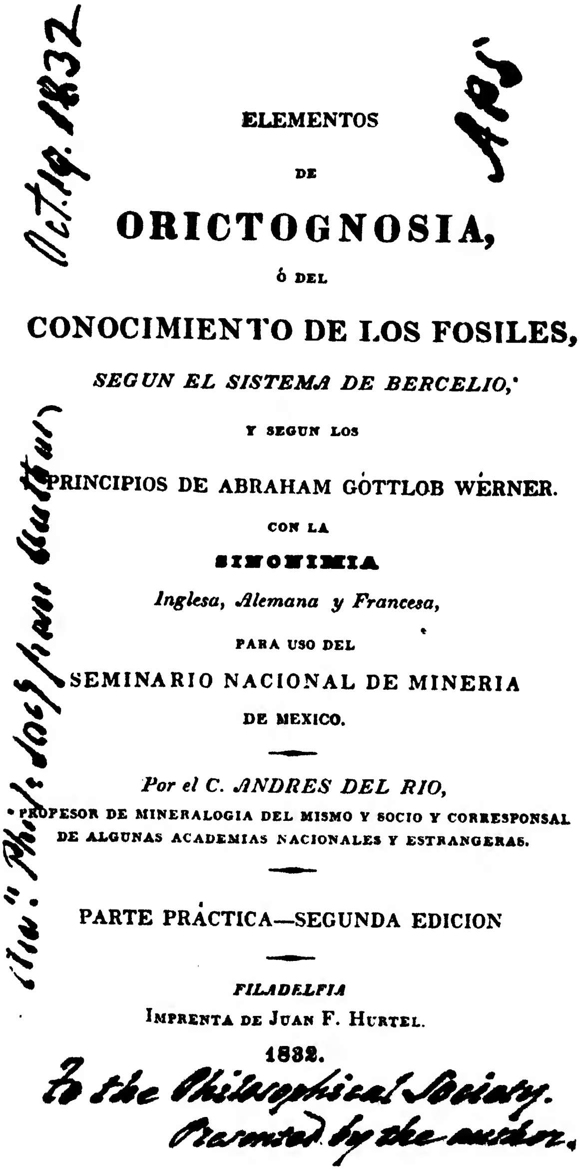
Dr. Ernst Wittich, German Ambassador to Mexico, has pointed out that Baron von Humboldt was also led into the same error, for the specimen in the *Museum für Naturkunde* in Berlin is labeled in the Baron's handwriting: "Brown lead ore from the veins of Zimapán in northern Mexico. Lead chromate. M. del Río thought he had discovered a new metal in it, which he named erythronium, then panchromium; later he realized that it was ordinary chromium." The label was later corrected by Gustav Rose to read: "*Vanadiumbleierz*" (vanadium lead ore)(*29*).

Another circumstance which helped to shake del Río's confidence in his own work was the analysis of this mineral which Collet-Descotils, a friend of Vauquelin, published in 1805 (*13*). When Collet-Descotils concluded that the supposed new metal was merely chromium, del Río warmly defended his own prior claim to the "discovery" of *chromium* in the brown lead ore (*14*).

The details of Sefström's discovery of vanadium in soft iron from the Taberg Mine in Småland, Sweden, and of Wöhler's proof of the identity of erythronium and vanadium have already been related (*14*), (*15*), (*16*). Dr. Moles has emphasized the fact that del Río's own excessive modesty and scientific caution led him to renounce the discovery of the new element before the analysis of Collet-Descotils had been published.

Unaware of the shipwreck which had prevented Humboldt from giving full publicity to the discovery of erythronium, del Río wrote in 1832 in his "Elements of Oryctognosy": "When he left Mexico, I gave him . . . a copy in French of my experiments in order that he might publish them. If he had judged them worthy of public attention, they would have excited the curiosity of chemists, and *the discovery of the new metal would not have been delayed for thirty years*, which is the objection now unjustly made against me. He did not even show Descotils the copy of my experiments, for, since he [Descotils] was a chemist, he would have appreciated them better, would have repeated them, and with his knowledge of chromium, which I lacked, it would have been easy for him to decide that it was a distinct metal" (*7*), (*17*). Since at that time chromium must have been a novelty even in Europe and since it often required ten or twelve years for the news of European discoveries to reach Mexico (*22*), del Río should not be criticized for having been uninformed as to the properties of this metal.

For a number of years del Río taught not only mineralogy and mining, but also Spanish and French, and served as one of the editors of the *Gaceta de México*, to which he contributed many articles, both literary and scientific. In order that his students might "be proud of a country that offers so many opportunities for admiring Nature," del Río added to his translation of Karsten's "Mineralogical Tables" a number of descriptions of



Oct. 19. 1832

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ELEMENTOS
DE
ORICTOGNOSIA,
ó DEL
CONOCIMIENTO DE LOS FOSILES,
SEGUN EL SISTEMA DE BERCELIO,
Y SEGUN LOS
PRINCIPIOS DE ABRAHAM GÖTTLOB WERNER.
CON LA
SINONIMIA
Inglesa, Alemana y Francesa,
PARA USO DEL
SEMINARIO NACIONAL DE MINERIA
DE MEXICO.

Por el C. ANDRES DEL RIO,
PROFESOR DE MINERALOGIA DEL MISMO Y SOCIO Y CORRESPONSAL
DE ALGUNAS ACADEMIAS NACIONALES Y ESTRANGERAS.

PARTE PRÁCTICA—SEGUNDA EDICION

FILADELFIA
IMPRENTA DE JUAN F. HURTEL.
1832.

Rec'd: "Phil: Soc:" from Author

To the Philosophical Society.
Presented by the author.

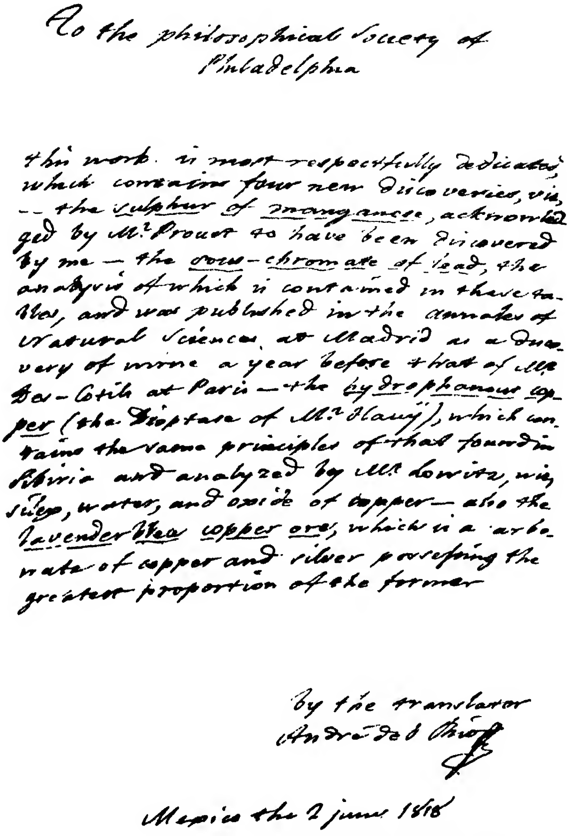
Courtesy Am. Philosophical Soc.

TITLE PAGE OF DEL RÍO'S "ELEMENTS OF ORYCTOGNOSY" WRITTEN ACCORDING TO THE SYSTEM OF BERZELIUS AND THE PRINCIPLES OF A. G. WERNER

minerals from "this America" and "the other America." Since a French reviewer (*5*) had criticized him in 1797 for not completely adopting the new nomenclature proposed by Lavoisier, del Río wrote in 1804, "Usage has accepted *oxígeno* in place of *arcicayo*, *oxido* in place of *cayo* . . . and I have adjusted the nomenclature in conformity with it" (*9*). In 1805 he published the second volume of his "Elements of Oryctognosy."

In the following year he established at Coalcomán, Michoacán, the first ironworks in Mexico, which, however, were destroyed during the insurrection of 1811 (*1*), (*3*). An incident related by Ramírez (*1*) illustrates the fairness of del Río's judgment. When the master blacksmith at the Coalcomán ironworks, who regarded his own skill as superior to that of del Río, asked for the use of an experimental furnace, del Río granted the request. Although the experiments resulted disastrously, del Río's report merely stated: "Pillado did not succeed very well, but these are the first experiments."

Von Humboldt, who was greatly interested in del Río's pumping engine, described it as follows: "This engine, which is the first of this kind constructed in America, is much superior to those in the mines of Hungary; it was constructed according to the estimates and plans of Señor del Río, professor of mineralogy of Mexico, who has visited the most famous mines of Europe and who possesses most thorough and varied erudition; and Mr. Lachaussée, an artisan native of Brabant, a man of marked ability, built it. . . . It is unfortunate that this beautiful engine, whose throttle valve is provided with a special mechanism, is set up in a place where it is difficult to get enough water to run it continuously. . . ." The Baron then explained that the amount of water had been estimated in an unusually rainy year, and added that "Señor del Río, when he arrived in New Spain, had no other aim than that of proving to Mexican mine operators the effect of such machines and the possibility of making them in this country. . . " (*6*). Ramírez (*1*) stated, however, that del Río had predicted the diminution of



To the philosophical Society of
Philadelphia

this work is most respectfully dedicated
which contains four new discoveries, viz.
— the sulphur of manganese, acknowledged
by Mr. Proust to have been discovered
by me — the sous-chromate of lead, the
analysis of which is contained in these tables,
and was published in the Annales of
Natural Sciences at Madrid as a discovery
of mine a year before that of Mr
Des-Cotils at Paris — the hydrophanous copper
(the Dioptase of Mr Haüy), which contains
the same principles of that found in
Sibiria and analyzed by Mr Lowitz, viz.
silex, water, and oxide of copper — also the
lavender bleu copper ore, which is a carbonate
of copper and silver possessing the
greatest proportion of the former

By the translator
Andrés del Rio

Mexico the 2 june 1818

Courtesy Am. Philosophical Soc.

In a presentation copy of his translation of Karsten's "Mineralogical Tables," del Río wrote as follows: "To the Philosophical Society of Philadelphia this work is most respectfully dedicated, which contains four new discoveries, viz.—the *sulphur of manganese*, acknowledged by Mr. Proust to have been discovered by me—the *sous-chromate of lead*, the analysis of which is contained in these tables, and was published in the Annales of Natural Sciences at Madrid as a discovery of mine a year before that of Mr. Des-Cotils at Paris—the *hydrophanous copper* (the Dioptase of Mr. Haüy), which contains the same principles of that found in Sibiria and analyzed by Mr. Lowitz, viz., silex, water, and oxide of copper—also the *lavender bleu copper ore*, which is a carbonate of copper and silver possessing the greatest proportion of the former, by the translator André del Río, Mexico the 2 June 1818."

water supply, but had been unable to prevent the deforestation which had caused it.

In 1820 deputies were appointed to the Spanish court. H. H. Bancroft stated in his "History of Mexico" that this election "took place with no little disorder" and that ". . . the choice fell almost exclusively on ecclesiastics and lawyers, with a sprinkling of soldiers, merchants, and men of no particular calling, among whom were three natives of Spain" (*18*). One of the latter was Andrés Manuel del Río, who pleaded earnestly for the independence of his adopted country. Although Elhuyar resigned his position and returned to Spain during the struggle, del Río was in sympathy with the new cause (*19*) and, according to Maffei and de la Rua Figueroa (*1*), was one of the few deputies to vote for absolute independence.

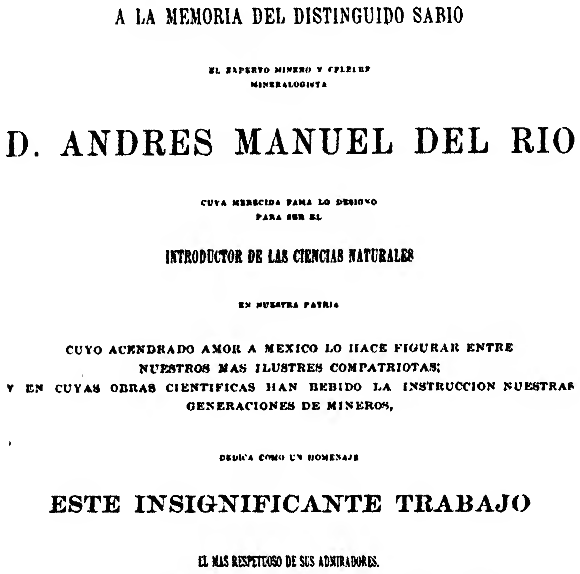
During his visit to Spain, del Río was offered the directorship of the mines of Almadén and of the Museum of Sciences in Madrid, but he preferred to return to Mexico. While he was in Bordeaux, Señora de Elhuyar said to him, "Where are you going, del Río? Don't you know that Mexico has become independent?" "Yes," replied del Río, "and I am going home to my country" (*1*). Because of his loyal friends and eager, intelligent students, his splendid collection of minerals from both hemispheres, the undiscovered wonders of the new world, and the charm of his virtuous Mexican wife, del Río had come to regard Mexico as his homeland. Perhaps another incentive for his return was the impressive structure for the School of Mines which had been completed in 1813, and which Mr. Beulloch, a contemporary English traveler, described as follows (*20*):

"The edifice in which it is located excels in its dimensions and in the beauty of its architecture all those in Europe destined for the same purpose. It was erected at great cost [$1^1/_2$ million pesos] and amply provided with everything necessary for the mine owners and other rich inhabitants." Earthquakes soon damaged the noble structure to such an extent that by 1830 extensive repairs were needed. The architect took the high building apart, placed the stately columns in the patio, and put them back in place without losing a single piece (*7*).

In 1824 del Río published an analysis of a gold-rhodium alloy from the smelting house in Mexico which was similar to the gold-palladium ingot previously reported by Joseph Cloud, director of the Philadelphia Mint (*21*). Three years later he published a translation of Berzelius' "New mineral system" (*22*). He served for some time on a committee appointed to inspect the money and improve working conditions at the Mint.

In acknowledgment of his allegiance, the new government, which expelled most Spaniards from Mexico in 1828, made an exception in the case of del Río. Nevertheless, he preferred to share the fate of his fellow-countrymen and therefore spent four years of voluntary exile in Philadelphia. In the preface to the second edition of his "Elements of Oryctognosy," published in Philadelphia in 1832 at the expense of the Mining Tribunal of Mexico, he wrote:

"Knowing by experience the happy disposition of Mexican youth for the study of these sciences, I wish in the last third of my life to consecrate to it the limited product of my efforts, immeasurably happy if I can some day be useful to a country where I have lived for thirty-five years, receiving every kind of distinction. If the result is not proportional to my high aim, it will at least be admitted that I aspire to manifest in the only manner possible to me my gratitude for the distinguished favors with which the Mexicans have honored me; my only merit is to be thankful" (*17*).



A LA MEMORIA DEL DISTINGUIDO SABIO

EL EXPERTO MINERO Y CELEBRE
MINERALOGISTA

D. ANDRES MANUEL DEL RIO

CUYA MERECIDA FAMA LO DESIGNO
PARA SER EL

INTRODUCTOR DE LAS CIENCIAS NATURALES

EN NUESTRA PATRIA

CUYO ACENDRADO AMOR A MEXICO LO HACE FIGURAR ENTRE
NUESTROS MAS ILUSTRES COMPATRIOTAS;
Y EN CUYAS OBRAS CIENTIFICAS HAN BEBIDO LA INSTRUCCION NUESTRAS
GENERACIONES DE MINEROS,

DEDICA COMO UN HOMENAJE

ESTE INSIGNIFICANTE TRABAJO

EL MAS RESPETUOSO DE SUS ADMIRADORES.

DEDICATION PAGE OF "THE MINERAL WEALTH OF MEXICO AND ITS PRESENT STATE OF DEVELOPMENT," WHICH S. RAMÍREZ WROTE FOR THE NEW ORLEANS EXPOSITION OF 1884.

Translation: "To the memory of the distinguished scientist, expert mine operator, and celebrated mineralogist, D. Andrés Manuel del Río, whose well deserved fame designated him to be the introducer of the natural sciences into our country, whose stainless love for Mexico makes him figure among our most illustrious fellow citizens, and from whose scientific books our generations of mine operators have imbibed instruction, this unimportant work is dedicated as a tribute by the most respectful of his admirers."

In his unassuming devotion to his teaching duties, del Río resembled John Dalton. One day in 1841, when a student knocked at the door of his classroom to announce a distinguished visitor, del Río asked the messenger to have the visitor wait for him. When the bell rang at the close of the class period, del Río greeted Señor Calderon de la Barca, minister plenipotentiary from the Court at Madrid. His Excellency, moreover, was not offended at the delay (*1*).

Del Río belonged to many scientific organizations of France, Germany, Great Britain, Mexico, and Spain, and was an active member of the American Philosophical Society and president of the Geological Society of Philadelphia. From 1830 to 1834 he attended the meetings of the American Philosophical Society, took part in the discussions, donated books which are still in possession of the Society's library, and presented papers for publication.

The translation of Karsten's Tables contains in del Río's handwriting the following note of presentation: "To the Philosophical Society of Philadelphia, this work is most respectfully dedicated, which contains four new discoveries—the *sulphur of manganese,* acknowledged by Mr. Proust to have been discovered by me—the *sous-chromate of lead* . . . the *hydrophanous copper* . . . also the *lavender . . . copper ore.*" This note was written in 1818, but in 1827 del Río wrote: "I thank Sr. Breithaupt for . . . believing me the first discoverer of manganese sulfide . . . I am indeed [discoverer] of that of los Mijes in the state of Qajaca [Oaxaca]; but we must be just Sr. Proust discovered that of Transylvania two years before" (*22*). Del Río added that at that time many European discoveries were not known in Mexico until ten or twelve years after publication. In the second edition of his "Elements of Oryctognosy," del Río wrote: "In a work such as this little can be called one's own: only a few articles belong to me, such as the manganese sulfide of Oaxaca, the brown lead of Zimapán, the mercury iodide of Casas Viejas, the blue silver of Catorce, and the zinc selenide of Culebras" (*17*).

His requests for a small specimen of "sulphuret of silver" and other minerals for analysis were granted by the Philosophical Society. At its meetings he must have met A. D. Bache, F. Bache, Robert Hare, Joseph Henry, G. W. Featherstonhaugh, and other contemporary American scientists. Ramírez (*1*) mentions a process of purifying mercury which del Río had learned from Professor Hare of Philadelphia.

In 1830 del Río read a paper on Becquerel's method of reducing silver ores (*23*). His paper (*24*) on the crystals developed in vermiculite by heat begins: "A pupil of the celebrated Werner, I have always been more of a Neptunian than a Plutonist, notwithstanding the many crystallizations produced in the dry way. A new instance which has come under my observation in the crystals of vermiculite has contributed materially to change my opinions . . . ."

Dr. Meigs had heated a specimen of vermiculite in a candle flame and had shown del Río the worm-like filaments which shoot out from it. Under the blowpipe, the Mexican scientist obtained from it oblique prisms nearly an inch long, which were also "crooked and worm-like." Vermiculite is a hydrous silicate generally produced by alteration of mica.

Between 1835 and 1837 several polemical articles by del Río and Charles U. Shepard, the well-known American mineralogist and collector of meteorites, appeared in the *American Journal of Science* (*25*).

In 1834 del Río was given the chair of geology in addition to that of mineralogy. Before returning to Mexico, he purchased for the Mining Seminary a splendid collection of shells and fossils collected by a Polish naturalist who had recently died in Philadelphia. In 1841 he published a manual of geology describing the fossil flora and fauna of the various rocks, with special emphasis on those found in Mexico (*7*), (*26*). Two years later del Río, then about seventy-eight years of age, served on a committee to study the manufacture of porcelain and determine whether or not the raw materials were available in the Republic. Their report, which was highly praised by the Bureau of National Industry, was published in *El Siglo XIX* on May 10, 1843, and a porcelain works was established at Puebla (*3*).

Two years later del Río was still serving as professor of mineralogy, but in the following year he asked for a substitute in order that he might complete the supplement to his textbook, which was to include discussions of the most recent discoveries made in Europe and the United States. According to Señor Ramírez (*7*), this was published in 1849 (*27*). In spite of failing eyesight, del Río continued, almost to the close of his life, to contribute to the literary and scientific periodicals of Mexico, yet in spite of his illustrious services, he was reduced to poverty in his old age (*28*). On March 23, 1849, he suffered a fatal cerebral attack.

Del Río's colleague, Don Joaquín Velázquez de León, said in his eulogy: "I still seem to see him leaving this college at the close of the day's teaching, with his book under his arm (for he used to say *that the support of science does not dishonor anyone*); surrounded at the doorway of the institution by the unfortunate and the destitute, sharing with them his meager salary, and returning to aid those who were already waiting for him at the doors of his home" (*1*). In 1877 a rich mining region of Chihuahua was named in his honor *the Andrés del Río canton*, with Batopilas as its capitol (*7*).

It is a pleasure to acknowledge the kind assistance of Miss Eva Armstrong of the Edgar Fahs Smith Memorial Library, the library of the American Philosophical Society, Dr. E. Moles and Señor A. de Gálvez-Cañero of Madrid, and Dr. F. B. Dains.

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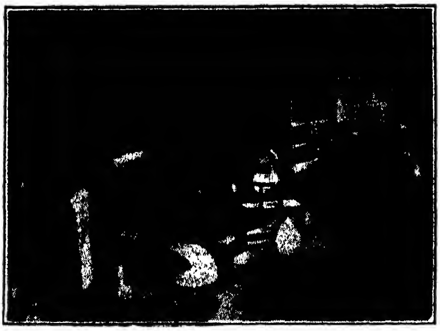


XIV. THE PLATINUM METALS

The earliest scientific descriptions of platinum are those of Dr. Brownrigg and Don Antonio de Ulloa in the middle of the eighteenth century. Rhodium, palladium, osmium, and iridium were discovered in 1803 and 1804, the first two by Dr. Wollaston and the others by his friend, Smithson Tennant. Thomson's "History of Chemistry" and Berzelius' correspondence and diary present a pleasing picture of these two great English chemists. Ruthenium, the Russian member of the platinum family, was discovered much later by Karl Karlovich Klaus, whose life story was beautifully told by the late Professor B. N. Menschutkin of the Polytechnic Institute of Leningrad.

. . . .

> *A successful pursuit of science makes a man the benefactor of all mankind and of every age (1).*

Platinum

Although platinum occurs as grains and nuggets in the alluvial sands of many rivers, there is only slight evidence of its use by ancient peoples. The pre-Columbian Indians, however, near the place now known as La Tolita, Esmeraldas, Ecuador (*39*), produced white alloys of gold and platinum, from which they made many little artifacts, some of which are now preserved in the University of Pennsylvania Museum in Philadelphia and the Danish National Museum in Copenhagen. Since platinum cannot be melted with any primitive source of heat, Paul Bergsøe (*40*) believes that a little gold was mixed with the grains of platinum in order to seal them together as the gold was melted, and that the sintered mass was then subjected to alternate heating and hammering.

Julius Caesar Scaliger
1484–1558

Italian physician, scholar, and poet. In 1557 he made a brief allusion to a refractory metal which was probably platinum. His son Joseph Justus Scaliger was a famous philologist.

In 1557 a famous Italian scholar and poet, Julius Caesar Scaliger, or della Scala, made what is probably the first definite allusion to platinum. In his well-known work "On Subtlety," Girolamo Cardano (1501–1576) had defined a metal as "a substance which can be melted and which hardens on cooling." In his *Exo-*

tericarum exercitationum liber quintus decimus de subtilitate ad Hieronymum Cardanum, Scaliger pointed out that such a definition would exclude mercury and also another metal, found between Mexico and Darien, "which no fire nor any Spanish artifice has yet been able to liquefy" (*41*), (*54*).

Charles Wood, a metallurgist and assayer, found in Jamaica some platinum from Carthagena, [Colombia], and in 1741 took some of it to his relative, Dr. Brownrigg. After preparing a thorough and accurate description of the metal and its properties, Dr. Brownrigg in 1750 presented these specimens to the Royal Society of London. The exhibit included the ore as found in Nature, the purified metal, the fused metal, and a sword with a pummel made partly of platinum (*2*).

DON ANTONIO DE ULLOA
1716–1795

Spanish mathematician, naval officer, and traveler. The log of his voyage to Peru published in 1748 contains a description of platinum.

SIR WILLIAM WATSON, 1715–1787

British physician, naturalist, and electrician who contributed many original papers and summaries of the work of others to the *Philosophical Transactions*. In 1750 he communicated Dr. William Brownrigg's paper on platinum to the Royal Society. This portrait was engraved by Thornthwaite after a painting by Abbott.

In 1735 the French and Spanish governments sent a scientific expedition to Peru and to Ecuador to measure a degree of meridian at Quito, close to the equator. One of the two naval officers appointed by Philip V to take charge of the expedition was the brilliant young mathematician, Don Antonio de Ulloa (1716–1795). The French ship on which he returned in 1744 was compelled to surrender to the British at the port of Louisburg, Cape Breton, but the English naval officers treated him with the utmost courtesy and kindness, preserved his scientific records, and guaranteed him a safe passage to England.

When he petitioned the Admiralty for the return of his papers, says Don Antonio de Ulloa, they "unanimously, and with pleasure, granted the contents of my memorial, nobly adding that they were not at war with the arts and sciences, or their professors." Upon his arrival in London, de Ulloa was introduced to Martin Folkes, the president of the Royal Society, and to many other distinguished men and was elected to membership in that society (*32*).

In 1746 de Ulloa returned to Madrid, and, with Jorge Juan, prepared for publication the memorable "Historical Account of the Voyage to South America," which was published in 1748 (*35*), (*55*), (*56*). In the preface to his "Astronomical and Physical Observations," Jorge Juan said that Ulloa regarded platinum as a peculiar metal and anticipated that there must be special mines of it just as there are of gold and silver (*55*).

De Ulloa described it as follows: "In the district of Chocò are many mines of Lavadero, or wash gold . . . several of the mines have been abandoned on account of the platina; a substance of such resistance that, when struck on an anvil of steel, it is not easy to be separated; nor is it calcinable; so that the metal, inclosed within this obdurate body, could not be extracted without infinite labour and charge . . . (*56*), (*57*)."

De Ulloa and Jorge Juan sent a dozen copies of this log to members of the Royal Society of London. On December 19, 1748, William Watson (later Sir William) wrote as follows: "Only last Wednesday I was delighted to receive the copies of your book which you intended for me and your other friends, for which I sincerely thank you . . . . On Thursday Mr. Folkes did not fail to present . . . the copy marked for the Royal Society . . . . The Society voted its special thanks to you both for the gift of a book so charged with curious, choice, and interesting information" (*58*).

Unfortunately, de Ulloa's many activities did not leave him time for a thorough investigation of the new metal. After studying the sciences and useful arts of several European countries, he returned to Spain and reorganized the Schools of Medicine and Surgery, established the textile industry, and developed the mercury mines of Almadén. In 1758 he was sent to Peru to superintend the mercury mines of Huancavelica.

When the Treaty of Fontainebleau gave Spain authority over Louisiana, Charles III in 1765 ordered Don Antonio to take possession. When he arrived at New Orleans in a heavy storm, the colonists gave him "a respectful, but cold and somber, greeting" (*59*). In his "History of Louisiana," Albert Phelps explained: "He was cold, reserved, and proud, but the source of his dignity—his reputation as a man of learning and science—was all unknown to Louisiana, and therefore his assumption of authority, unsupported by any appearance, was taken to be mere arrogance or pretention" (*60*). Another historian stated that "his scientific spirit, as often happens, led him to waste his time on trifling details" (*59*).

When his fiancée arrived from Peru, they were married at the Balize by the chaplain of the vessel which had brought her. This unceremonious procedure, together with de Ulloa's prolonged absence from New Orelans, brought fresh criticism from the colonists, and he was soon dismissed (*34*). N.-J. Thiery de Menonville, a contemporary French botanist and traveler, said, "I have heard much fault found with Don Uloa [sic], but all the subjects of complaint that were alledged against him were charges of familiarity unworthy of his rank, and a shabby meanness in his domestic concerns. He has never given room for anyone accusing him of injustice or cruelty . . . his excessive patience made him to be despised and dismissed" (*61*).

After serving for a time as commander of the fleet, de Ulloa returned to Spain. Joseph Townsend, a contemporary traveler, gave the following description of his visit to de Ulloa at Cadiz: "For my part, . . . I chiefly associated with Spaniards. Among these the principal was Don Antonio Ulloa, the well known companion of D. Georg Juan . . . . I found him perfectly the philosopher, sensible and well informed, lively in his conversation, free and easy in his manners . . . . This great man, diminutive in stature, remarkably thin and bowed down with age, clad like a peasant, and surrounded by his numerous family of children, with the youngest, about two years old, playing on his knee, was sitting to receive morning visitors . . . .

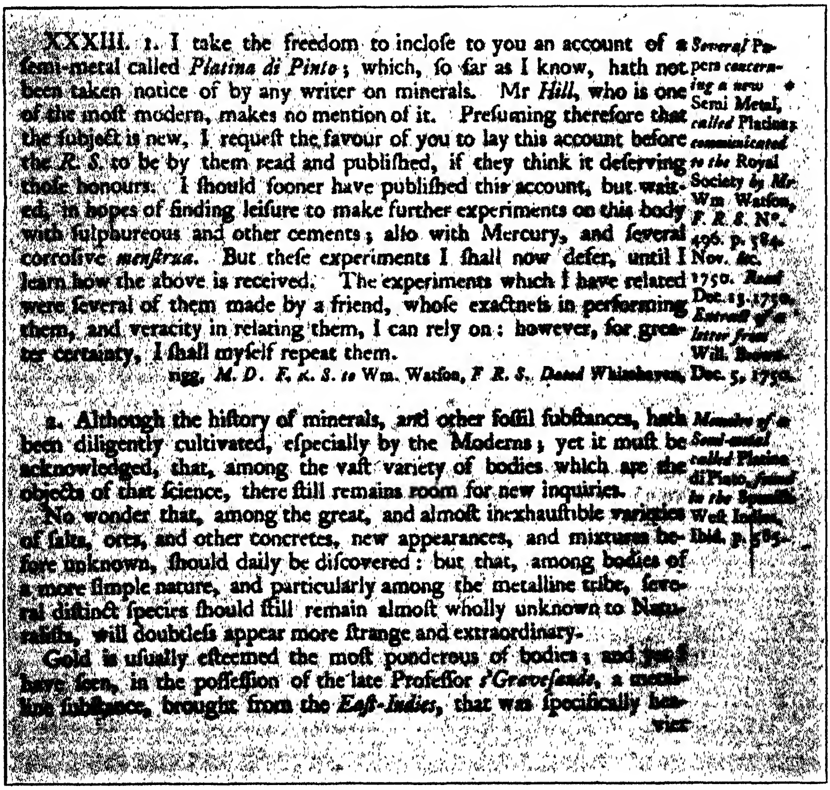
"The room was twenty feet long by fourteen wide, and less than eight feet high. In this I saw dispersed confused, chairs, tables, trunks, boxes, books, and papers, a bed, a press, umbrellas, clothes, carpenters' tools, mathematical instruments, a barometer, a clock, guns, pictures, looking-glasses, fossils, minerals, and shells, his kettle, basons, broken jugs, American antiquities, money, and a curious mummy from the Canary Islands . . . . When I went to take my leave of him, on quitting Cadiz, he presented me with his Natural History of South America, a work highly deserving to be translated" (*62*).

De Ulloa died on León Island near Cadiz on July 5, 1795. According to Sempere y Guarinos, he brought to Spain the first knowledge of electricity and artificial magnetism, and used a solar reflecting microscope, such as he had seen in England, to demonstrate the circulation of the blood in the appendages of fish and various insects. From his journeys, Ulloa brought back a knowledge of the cinnamon and rubber trees and of improvements in the arts of printing and binding. He also established the first cabinet of natural history and the first metallurgical laboratory in Madrid (*58*).

About two years after the log of de Ulloa's voyage had been published, Sir William Watson and Dr. William Brownrigg contributed to the *Philosophical Transactions* a more detailed description of platinum. William

Brownrigg was born at High Close Hall, Cumberland, on March 24, 1711. He studied medicine in London and later in Leyden under Boerhaave, Albinus, and W. J. s'Gravesande, and began to practise in Whitehaven (*2*), (*63*), (*64*).

A paper read by Watson before the Royal Society on December 13, 1750, contained an excerpt from a letter, dated Whitehaven, December 5th of the same year, in which Dr. Brownrigg had mentioned some experiments which a friend of his had made on "the semi-metal called Platina di Pinto" (sic!), a substance which he had not found mentioned by any writer on minerals (*65*). Dr. Brownrigg regarded it as strange that such a simple substance "among the metalline tribe" should have remained unknown to naturalists. He pointed out that the principle, long accepted by assayers, that gold and silver may be purified from all other substances by cupella-



XXXIII. 1. I take the freedom to incloſe to you an account of a ſemi-metal called *Platina di Pinto*; which, ſo far as I know, hath not been taken notice of by any writer on minerals. Mr *Hill*, who is one of the moſt modern, makes no mention of it. Preſuming therefore that the ſubject is new, I requeſt the favour of you to lay this account before the *R. S.* to be by them read and publiſhed, if they think it deſerving thoſe honours. I ſhould ſooner have publiſhed this account, but waited, in hopes of finding leiſure to make further experiments on this body with ſulphureous and other cements; alſo with Mercury, and ſeveral corroſive *menſtrua*. But theſe experiments I ſhall now defer, until I learn how the above is received. The experiments which I have related were ſeveral of them made by a friend, whoſe exactneſs in performing them, and veracity in relating them, I can rely on: however, for greater certainty, I ſhall myſelf repeat them.

Several Papers concerning a new Semi Metal, *called* Platina; *communicated to the Royal Society by Mr* Wm Watſon, *F. R. S.* N°. 496. p. 584. Nov. &c. 1750. *Read* Dec. 13. 1750. *Extract of a letter from* Will. Brownrigg, *M. D. F. R. S. to* Wm. Watſon, *F. R. S. Dated Whitehaven*, Dec. 5, 1750.

2. Although the hiſtory of minerals, and other foſſil ſubſtances, hath been diligently cultivated, eſpecially by the Moderns; yet it muſt be acknowledged, that, among the vaſt variety of bodies which are the objects of that ſcience, there ſtill remains room for new inquiries.

No wonder that, among the great, and almoſt inexhauſtible varieties of ſalts, ores, and other concretes, new appearances, and mixtures before unknown, ſhould daily be diſcovered: but that, among bodies of a more ſimple nature, and particularly among the metalline tribe, ſeveral diſtinct ſpecies ſhould ſtill remain almoſt wholly unknown to Naturaliſts, will doubtleſs appear more ſtrange and extraordinary.

Gold is uſually eſteemed the moſt ponderous of bodies; and yet I have ſeen, in the poſſeſſion of the late Profeſſor *s'Graveſande*, a metalline ſubſtance, brought from the *Eaſt-Indies*, that was ſpecifically hea-

vier

Memoirs of a Semi-metal called Platina di Pinto, *found in the Spaniſh* Weſt Indies, ibid. p. 585.

FACSIMILE PAGE FROM VOLUME X OF THE *Philosophical Transactions Abridgment* SHOWING WILLIAM WATSON'S DESCRIPTION OF PLATINUM AND A LETTER FROM DR. BROWNRIGG ON THE SAME SUBJECT.

tion, did not apply to the new "semi-metal," for it, like gold, "resists the power of fire and the destructive force of lead." He added that this "platina" had been presented to him about nine years before by "a skilful and inquisitive metallurgist [Mr. Charles Wood] who met with it in Jamaica, whither it had been brought from Carthagena" (Colombia). Dr. Brownrigg believed it probable that "there is great plenty of this semi-metal in the Spanish West Indies, since trinkets made of it are there very common." He mentioned its high melting point and its refractoriness toward borax and other saline fluxes. "But the Spaniards," said he, "have a way of melting it down, either alone or by means of some flux; and cast it into sword-hilts, buckles, snuff-boxes, and other utensils."

Herrn Peter Joſeph Macquers
Doctors der Arzneygelahrheit von der Pariſer Facultät, Mitgliedes der königl. franz. Akademie der Wiſſenſchaften und der königl. Geſellſchaft der Arzneygelahrheit, Profeſſors der Chymie ꝛc.
Chymiſches
Wörterbuch
oder
Allgemeine Begriffe
der Chymie
nach alphabetiſcher Ordnung.
Aus dem Franzöſiſchen nach der zweyten Ausgabe überſetzt
und mit
Anmerkungen und Zuſätzen vermehrt
von
D. Johann Gottfried Leonhardi
der Pathologie und Chirurgie ordentlichem öffentlichen Profeſſor zu Wittenberg und der Leipz. Ökon. Geſellſch. Mitgliede.
Zweyte verbeſſerte und vermehrte Ausgabe.
Erſter Theil.
Von A bis C.
Leipzig,
in der Weidmanniſchen Buchhandlung, 1788.

TITLE PAGE OF THE GERMAN EDITION OF MACQUER'S CHEMICAL DICTIONARY

Pierre-Joseph Macquer, 1718–1784, was one of the first chemists to investigate platinum.

In about 1730, "Don Jorge de Villalonga, first viceroy of Santa Fé, was given a guard for his rapier and some buckles of platina, but was assured that it had not been sufficiently joined or made to coalesce and that it was a brittle metal, but much heavier than the gold with which it was associated in the mines of the province of Cítaro in the district of Chocó" (*66*).

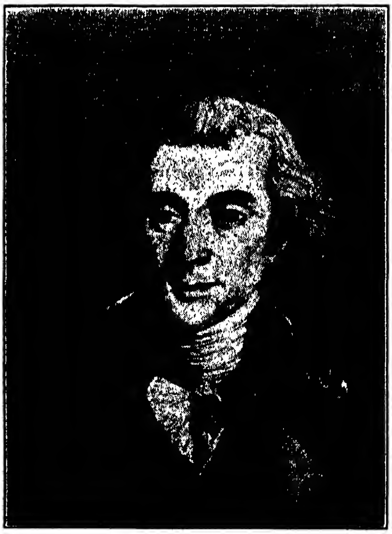
Sir William Watson said that he had seen this substance mentioned by no other author except de Ulloa. On February 13, 1750, Dr. Brownrigg wrote again to Watson, explaining that the experiments he had mentioned in his previous letter had been made by Mr. Charles Wood, who "was not ambitious of appearing in print," but had permitted Dr. Brownrigg to report his results to the Royal Society.

Dr. Brownrigg was always extremely modest about his discoveries, and preferred to live in comparative obscurity in Cumberland rather than to accept the wider opportunities of London. He died at Ormathwaite on January 6, 1800. A writer in *Gentleman's Magazine* said of him, "The poor and the rich had everywhere somewhat for which they thanked him, and health seemed only one of the blessings which he had to dispense" (*64*).

Sir William Watson was a distinguished physician, naturalist, and physicist. He was born in London on April 3, 1715, studied at the Merchant Taylors' School, and became apprenticed to an apothecary. He contributed to the *Philosophical Transactions* a large number of original papers and many reviews of the work of other scientists. His long series of brilliant experimental researches on electricity brought him great renown. For many years he served as physician to the Foundling Hospital in London. He was knighted in 1786 and died on May 10th of the following year.

ANTOINE BAUMÉ
1728–1804

French pharmacist and chemist. Author of a "Chymie expérimentale et raisonnée" in which he discussed chemical apparatus, chemical affinity, fire, air, earth, water, sulfur, gypsum, alum, clay, niter, gunpowder, borax, arsenic, glass, porcelain, and the common acids, alkalies, metals, and ores used in 1773. His hydrometer scale is still used. He was one of the first chemists to investigate platinum.



BERTRAND PELLETIER
1761–1797

French chemist and pharmacist who investigated the arsenates, phosphates, and phosphides of many metals, studied the action of phosphorus on platinum, and devised new methods for making soap and refining metal for clocks. He served as inspector of the hospitals in Belgium. His son, Joseph Pelletier (1788–1842), and Joseph Caventou discovered quinine, cinchonine, strychnine, and brucine.

The most distinguished chemists in Europe soon became intensely interested in platinum. Among those who published papers on it may be mentioned: H. T. Scheffer (*42*), Bergman and Berzelius in Sweden; Lewis in England; Marggraf in Germany; and Macquer, Baumé, Buffon, Guyton, Delisle, Lavoisier, and B. Pelletier (*43*), in France.

In 1752 H. T. Scheffer published a detailed scientific description of platinum, or "white gold," as he called it, and, with the aid of arsenic, succeeded in fusing it (*42*). Henric Theophil Scheffer was born in Stockholm on December 28, 1710, where his father was secretary to the Royal Board of Mines. After serving an apprenticeship under Georg Brandt, he established his own laboratory and made trips to the mines to learn firsthand the close connection between smelting and assaying.

In his eulogy, A. F. Cronstedt told the members of the Swedish Academy of Sciences how Scheffer became interested in platinum: "In his time," said Cronstedt, "a new metal happened to be discovered, which had evidently not been found in two thousand years, and it was most fitting that the first investigation of such a rare substance should fall to this man who was worthy of it.

"Your literary member, Herr Rudensköld [Ulrik Rudenschöld, 1704–1765], brought this honor to him and to us; for no sooner had Mr. Watson in London let Herr Bose [Georg Matthias Bose, 1710–1761] in Wittenberg know that something resembling a metal of unknown properties had been brought over from America, under the name of *Platina di Pinto*, until Herr Rudensköld arranged to get some of it through his acquaintances in Spain.

"The little bit that came," said Cronstedt, "he handed over to Scheffer, who, driven by his customary zeal, soon solved the mystery of its nature, and showed in a paper that it was a peculiar metal, different from all others, almost infusible when alone, just as noble as gold, and less pliable. He anticipated Mr. Lewis, who made experiments on a greater quantity of it and later published the results of them in the *Transactions of the British Scientific Society* [*Philosophical Transactions of the Royal Society* (*67*)]; but during the investigation neither was aware of the other's manipulations and conclusions, wherefore each of them established a special property in addition to what they in all other respects found to be identical.

"Our Scheffer," said Cronstedt, "who rejoiced over this incontrovertible evidence, found, however, an error in denoting the specific gravity of the many alloys which Mr. Lewis prepared from platinum and other metals; wherefore he corrected them in the *Handlingar* of this Society in a manner which bears witness that the love of truth did not turn the head of the person who found it" (*68*).

Scheffer died on August 10, 1759. As Cronstedt said, "he sought diligently to follow the path that leads to the right goal after death; for he could not harbor the false doctrine that gold, which hinders and leads astray, or panaceas alleged to prolong life can serve as remuneration for piety" (*68*).

In 1772 Baron Carl von Sickingen made extended researches on platinum and rendered it malleable by alloying it with silver and gold, dissolving the alloy in aqua regia, precipitating the platinum with ammonium chloride, igniting the ammonium chloroplatinate, and hammering the resulting finely divided platinum to make it cohere (*69*). His researches on this subject were not published until 1782 (*70*). Two years later F. C. Achard prepared the first platinum crucible by fusing platinum with arsenic and volatilizing off the arsenic (*69*).

The Marqués de los Castillejos presented the Basque Society of Friends of their Country with a large quantity of platinum. The *Extractos* of this Society published William Lewis's dissertation on this metal with the editorial note: "The Commission has made several tests according to this information and has succeeded in applying the use of this metal to the adornment of the handles of several razors and knives, giving it by admixture various tints of golden or yellow color" (*66*). After a thorough investigation of this metal at the Vergara Seminary, Pierre-François Chabaneau (or Chavaneau) succeeded in making pure platinum malleable (*66*).

Professor James Lewis Howe, author of an excellent bibliography of the metals of the platinum group, and Louis Quennessen, head of the firm of Des Moutis and Company, platinum refiners, have reviewed Chabaneau's contributions (*71*), (*72*), (*73*). Chabaneau was born at Nontron, Dordogne, in 1754. An uncle, a monk of the order of St. Anthony, encouraged him to study theology. Although Chabaneau was brilliantly successful in his studies, metaphysical speculations were so distasteful to him that he antagonized his teachers and was expelled from the school.

His penniless condition aroused the sympathy of the Abbé La Rose, director of a Jesuit college at Passy, who offered him the chair of mathematics. Although he scarcely knew arithmetic, Chabaneau, then only seventeen years old, was compelled by dire need to accept this unsuitable position. Studying by firelight every night in preparation for the next day's teaching, he mastered arithmetic, algebra, and geometry, and soon became deeply interested in physics, natural history, and chemistry.

At the age of twenty years he began to give a course of public lectures. Among his auditors were the sons of the Count of Peñaflorida, who had sent them to France to study and to select professors for the recently founded Vergara Seminary. They finally induced Chabaneau to go to Vergara to teach French and physics.

Don José Celestino Mutis mentioned in 1774 two portrait medallions of the King made by Don Francisco Benito, engraver at the Royal Mint in Santa Fè [Colombia]. One of these was made of an alloy containing equal parts of copper and platinum, the other of pure platinum (*74*). Two letters of Don Fausto de Elhuyar, long preserved with the Mutis manuscripts at the Botanical Garden in Madrid, show that he collaborated with Chabaneau in the researches on platinum. Writing from Vergara to his brother

Don Juan José in Bogotá on March 17, 1786, Don Fausto described their process in detail, and estimated the value of platinum as less than that of silver. From the other letter, written from Paris to Don Juan José on May 19th of the same year, it is evident that Chabaneau and the two Elhuyar brothers kept this process secret (*75*), (*76*).

Soon after this, King Charles III created for Chabaneau a public chair of mineralogy, physics, and chemistry at Madrid, lodged him in one of the royal palaces, and provided him with a valuable library and a luxurious laboratory (*72*), (*73*).

The Marqués de Aranda had the government turn over its entire supply of platinum to Chabaneau for his difficult and puzzling researches. When Chabaneau removed the gold, mercury, lead, copper, iron, etc., he thought he had a single metal, platinum. As a matter of fact, however, he was still dealing with six metals, for rhodium, palladium, osmium, iridium, and ruthenium had not yet been discovered. Small wonder that he oftentimes became discouraged by contradictory results. Sometimes the platinum was malleable and at other times it was brittle (alloyed with iridium); sometimes it was incombustible and nonvolatile and at other times (when an osmium alloy happened to be present) it burned and volatilized.

JOSÉ CELESTINO MUTIS
1732–1808

Spanish botanist, physician, and ecclesiastic who devoted his life to studying the natural history of northern South America. He investigated the cinchona (or chinchona) forests of Colombia (New Granada) and collaborated with Don Juan José de Elhuyar in developing its mines. He stated that the gold in the ores of Chocó cannot be spearated from the platinum except by amalgamation (*87*).

When Chabaneau began to work on other subjects, the patient Marqués de Aranda encouraged him to turn again to the great research on "white gold." Even when Chabaneau finally lost his temper and destroyed his apparatus and preparations, the Marqués still urged him not to lose confidence. Three months later, the Marqués found on a table in his home a ten-centimeter cube of metal. Attempting to pick it up, he said to Chabaneau, "You are joking. You have fastened it down." The little ingot weighed 23 kilograms; it was malleable platinum! Although the Marqués de Aranda had previously handled platinum only in the spongy form, Chabaneau had compressed a very pure platinum sponge, while hot, at the moment of its formation, and hammered it, while white hot, until it cohered.

The King, who had often come to the laboratory to watch the progress of the experiments, had a commemorative medal struck in platinum, and granted Chabaneau a life pension on condition that he remain in Spain. The letters-patent bearing the date 1783 establish Chabaneau's priority in this discovery (*72*).

Realizing that the very infusibility of platinum would lend value to objects made from it, Chabaneau and Don Joaquín Cabezas purified it, worked it, and carried on a lucrative business in the sale of platinum ingots and utensils. Thus began what Don Juan Fages y Virgili has called "the platinum age in Spain" (*66*). In 1799 Clavijo Fajardo, director of the Royal Laboratory of Natural History, asked the Minister for forty pounds of purified platinum and three arrobas (1 arroba = 25 pounds) of the native platinum grains for the use of Don Luis (Joseph-Louis) Proust for making crucibles and other utensils, and the government granted even more of it than was requested (*66*). Thus in a single laboratory in Madrid, "forty-six kilograms of platinum in grains and eighteen and one-half of the same purified were brought in in one day, that is to say, more platinum than we possess today [1909] in all the official laboratories in Spain" (*66*). Some of the platinum extracted from the gray sand which Don Antonio de Ulloa had brought from America was made into a magnificent communion cup for the chapel of the Royal Palace in Madrid (*77*).

Late in life Chabaneau renounced his pension in order to seek rest and restoration of his health near his native village. He died in 1842 at the age of eighty-eight years. Jules Delanoue, a contemporary, described him as "a fine-looking old man, with pleasing and regular features, bearing much resemblance to those of our good and lamented Béranger. His conversation was charming and always instructive. Friend and contemporary of Volney, of Cabanis, of Lavoisier, he was nourished upon their ideas and imbued with their spirit, and they were pleasingly reflected in his conversation" (*72*), (*73*).

When Chabaneau took some of his ingots to Paris, M. Jeanety made from them some beautiful pieces of jewelry and became so interested that he gave up his craftmanship in gold and silver to devote all his time to the working of platinum (*78*). Guyton-Morveau, Sir Joseph Banks, and some of the scientists in Sweden and the Netherlands ordered from him their platinum crucibles and ingots. Jeanety also made platinum snuff-boxes, watch-chains, spoons, toothpick boxes, blowpipes, and a set of buttons (*78*), (*79*). The prices were lower than for the corresponding articles in gold.

In reporting Jeanety's process to the French Bureau of Consultation in

1792, C.-L. Berthollet and Bertrand Pelletier stated that the gold from the Novitá and Citaría mines north of Chocó was separated from the platinum by sorting or by amalgamation. Since platinum could be used to alloy and adulterate gold, and since such alloys resisted parting, the Spanish government ordered that the platinum be thrown into the rivers. "The Chocó gold," said Berthollet and Pelletier, "is then sent to be coined in the two mints at Santa Fé, to those in Bogotá and Popayán, where any platinum which may have remained with the gold is again sorted out. Royal officers guard it, and when there is a certain quantity of it, they come with witnesses to throw it into the Bogotá River two leagues from Santa Fé and into the Cauca River one league from Popayán. The platinum always occurs in little grains; some of them, however, are quite large; there is even one in the cabinet of the Vergara Academy of the size of a pigeon's egg" (*78*).

When J.-B. Boussingault had charge of the metallic mines of Colombia, the Congress of that country voted that a platinum equestrian statue of Bolívar be erected in Bogotá. Charged with the duty of executing this order, Boussingault drew up a report showing that the production of all the mines in the country would be insufficient for this purpose and that it would be impossible to cast a statue from this refractory metal. On the advice of a superior official, he withheld the report, however, and, to shield the lawmakers from embarrassment, merely agreed to carry out the commission to the best of his ability. When the Congress had had time to forget about the statue of Bolívar, the two kilograms of platinum which had been carefully saved were made into apparatus for the laboratory of chemical engineering (*80*).

In 1801 Robert Hare, then only twenty years old, described before the Chemical Society of Philadelphia his oxyhydrogen blowpipe, with which he could fuse platinum. Two years later he reported to the American Philosophical Society that he had succeeded in volatilizing this metal (*81*). Hare's student, Joachim Bishop, later founded the American platinum refining industry (*82*). It was not until after the experiments of Wollaston, however, that the working of platinum became easy (*3*). William Hyde Wollaston, the son of an Episcopal clergyman, was born at East Dereham, Norfolkshire, England on August 6, 1766. His childhood was not a lonely one, for he had fourteen active brothers and sisters. After studying at Cambridge, he received his medical degree at the age of twenty-seven years. Although he practiced his profession for a time at Bury St. Edmunds,* he retired in 1800 and went to live in London, in order that he might devote all his time to physical science (*4*).

For half a century after its discovery platinum had few uses because of the difficulty of working it. Dr. Wollaston found, however, that spongy

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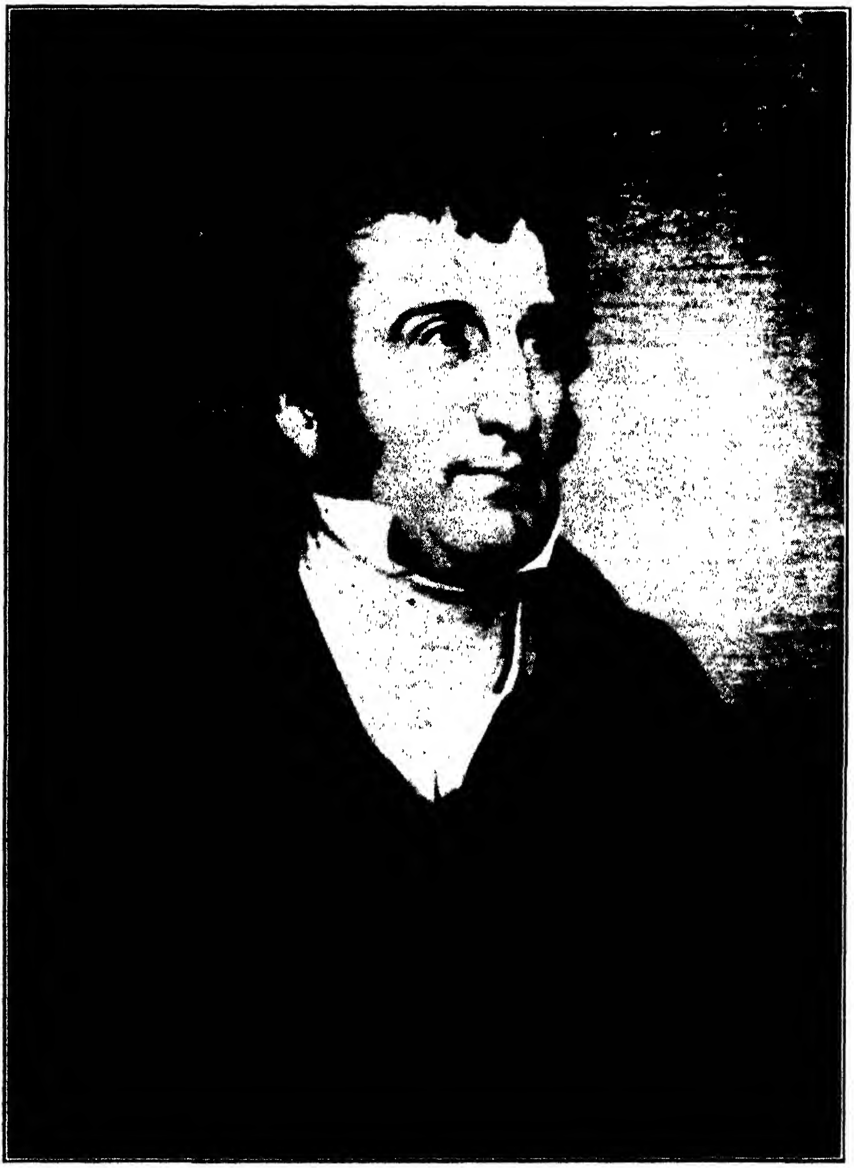
* John Winthrop the Younger once attended grammar school at this place.



Courtesy Edgar Fahs Smith Memorial Collection

ROBERT HARE
1781–1858

Professor of chemistry at the University of Pennsylvania. At the age of twenty years he invented the oxy-hydrogen, or compound, blowpipe, with which he fused and volatilized platinum and other refractory substances. He was most ingenious in devising chemical apparatus.

platinum becomes malleable when strongly compressed and that it can be annealed and hammered. This process made possible the widespread use of the metal for laboratory apparatus, and the income from it enabled Wollaston to retire from his medical practice at the early age of thirty-four years and devote the rest of his life to scientific research. He specified the exact composition of the aqua regia which would dissolve the platinum without dissolving the iridium, and the proper method of expelling the ammonium chloride without making the fine particles of platinum cohere. The pulverizing was done with the hands and with a wooden mortar and pestle, for harder surfaces burnished the platinum so that it could not be welded. The powder was then thoroughly washed with water, and, while still wet, strongly compressed in a mould, heated in a wind furnace, and struck, while hot, with a heavy hammer.

On April 22, 1813, Berzelius wrote from Stockholm to Dr. Marcet of London:

> When you see Dr. Wollaston give him a thousand compliments from me and then ask him if it would not be possible to have a little malleable platinum, not separated from its natural alloy with palladium, rhodium, etc., to make a crucible. The crucibles I have bought recently from Cary are of a metal noticeably purer than those which I formerly had, and for that very reason infinitely more susceptible to attack by other substances (*5*).

About two weeks later Dr. Marcet replied:

> Wollaston laughs at the idea that you want him to get you some impure platinum. He asks me to suggest that you alloy pure platinum with a little silver, as the surest means of increasing its durability (*6*).

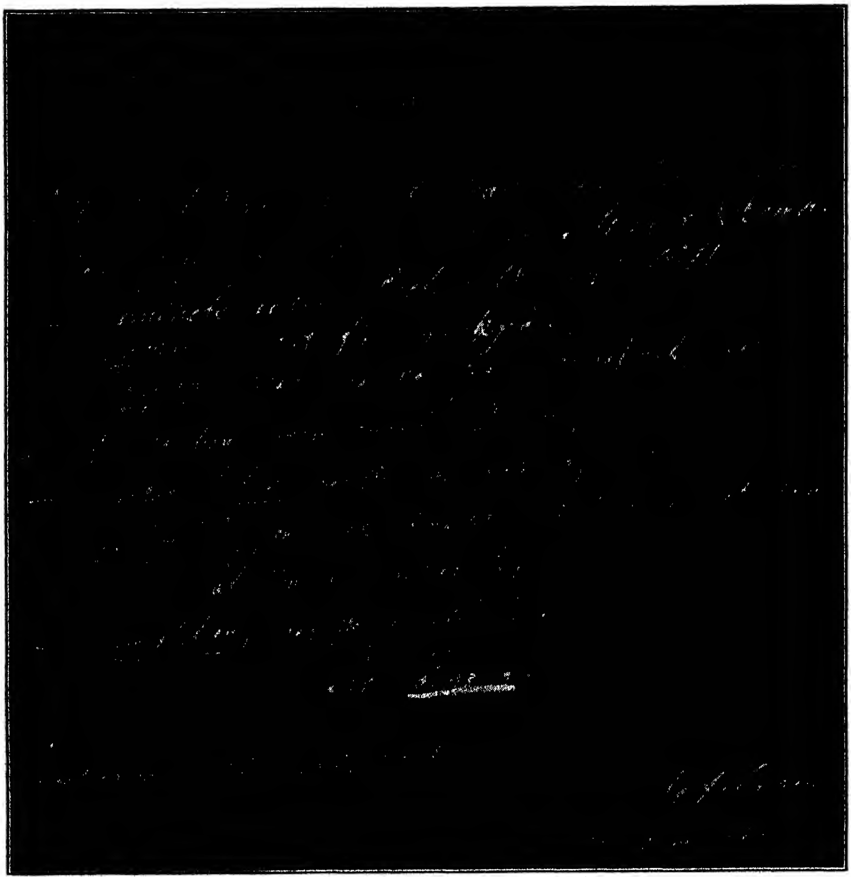
On February 24, 1829, Berzelius wrote to Eilhard Mitscherlich, "Wollaston's death grieves me. His specifications for making platina pliable were circulated at the same time as the news of his death. As I got iridium to cohere in an analogous manner, I was struck all the more by his simple method, went out into the laboratory, where I had a wet filter with platina on it, partly washed, which I pressed in a vice, dried, and ignited over a spirit lamp in a small platina crucible, and got it so coherent that it could no longer be broken with the fingers and could easily be cold-hammered. That's as far as I have yet gone. That was ten minutes' work, then I had to let it wait for a better time" (*83*).

That Berzelius made good use of Wollaston's process is evident from his letter to Wöhler written on May 1, 1829:

> We are now re-casting all our old soldered platinum crucibles by Wollaston's method of making platinum pliable; it goes like a dance. I think Wollaston must have laughed inside over the many elaborate methods which have been used in vain for this purpose, when his is so simple. It seems that by heating the bottom of the crucible glow-

ing hot in Sefström's forge, the formation of bubbles can be entirely prevented (7).

In preparing solid platinum from its powder, Wollaston foreshadowed modern methods of powder metallurgy, by which the powders of refractory



Edgar Fahs Smith Memorial Collection, University of Pennsylvania

A PAGE FROM SEFSTRÖM'S LABORATORY NOTES*

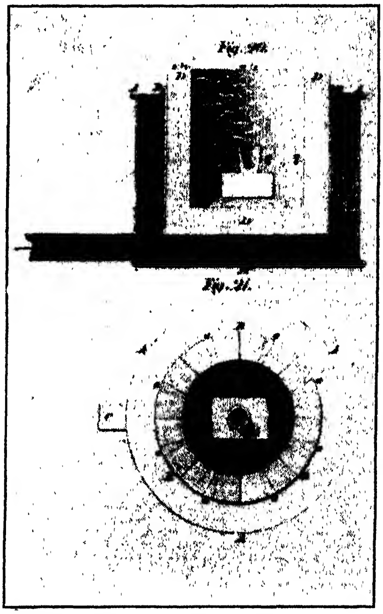
Translation: Cinchona reactions. 5 lbs. cortex Peruvian, first quality, with the sea captain Ripa from Amsterdam, belongs to Mazer and Co. Board of Health, minutes for Sept. 16, 1816. Bark very fine dark gray. Infusion clear, quite weak quinine taste, gave with iron solution a dark green precipitate. Antimony tartrate, very weak opalescence. Infusion of nutgalls, very heavy white precipitate like that of gelatin and nutgalls. Gelatin solution, faint opalescence. It is *no good*. Stockholm, Sept. 22, 1816. N. G. Sefström, M.D., Adjunct in Chemistry.

* The writer is deeply grateful to Miss Mary Larson of the Zoölogy Department at The University of Kansas and to Mr. Einar Bourman for the translation of this letter from the Swedish and for assistance in securing Swedish illustrations.

metals, such as tungsten, molybdenum, tantalum, and columbium, can be fabricated into useful articles (*84*), (*86*).

The technical working of massive platinum should be ascribed, however, to Thomas Cock, a brother-in-law of the platinum-refiner, P. N. Johnson, rather than to Wollaston. Cock worked out the process in William Allen's laboratory at Plough Court and, at Allen's request, communicated it to Wollaston (*51*). According to G. Matthey, P. N. Johnson was the first to manufacture platinum on a commercial scale and the first to prepare a large and perfect sheet of the pure metal. James Lewis Howe has stated that Chabaneau's process was rediscovered by Knight and possibly also by Cock (*72*).

In his lectures in 1817, W. T. Brande stated that platinum "may be considered as the exclusive product of South America" (*46*). In 1819, however, a white metal was observed in the gold placers on the eastern, or Siberian, slopes of the Urals, south of Ekaterinburg (Sverdlovsk) (*69*). In 1822 I. I. Varvinskij, director of the Gold-smelting Laboratory of Ekaterinburg, showed that it contained platinum, and V. V. Liubarskij, an assayer of St. Petersburg, later proved it to be osmiridium. In 1824 platinum was discovered north of Ekaterinburg in the Urals (*36*). The late B. N. Menschutkin published in the JOURNAL OF CHEMICAL EDUCATION an excellent historical sketch of the Russian platinum (*36*). In 1828 the Russian government authorized the coinage of large amounts of Siberian platinum acquired from Count Demidoff (*85*).



From Berzelius' "Lehrbuch der Chemie"

N. G. SEFSTRÖM'S PORTABLE EIGHT-BLAST FORGE

Fig. 20. Vertical section. Fig. 21. Transverse section.

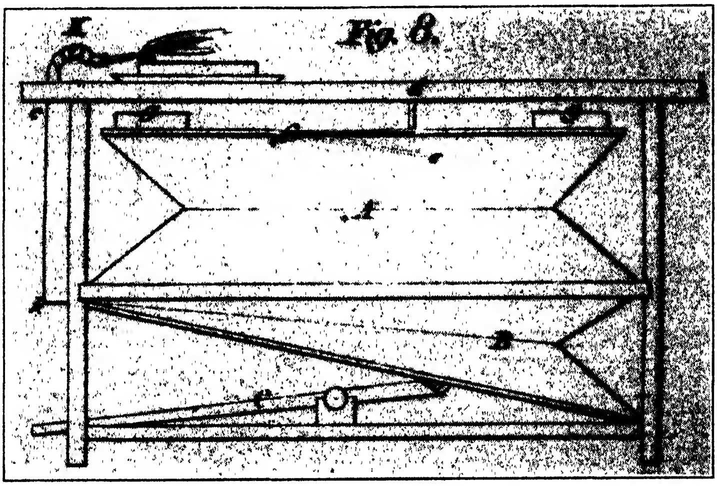
a . . . a are the eight conical tuyères from the bellows. With small pieces of dust-free wood charcoal as fuel, Sefström melted platinum in this forge.

Palladium

As early as 1700, or more than a century before palladium was discovered, Brazilian miners became familiar with a natural alloy which they called *prata* (silver), *ouro pòdre* (worthless, or spoiled gold), or *ouro branco* (white gold) (*44*). In about 1780 a silver-white gold bar at the Sabará smelting-house broke into several pieces under the impact of the die.

This gold had come from St. Anna dos Ferros, near Itabira do Dentro, Minas (*44*). In 1798 José Vieira do Couto mentioned several localities in Brazil where a silver-white "platinum" was to be found. This was probably the alloy palladium-gold.

In 1803 Dr. Wollaston succeeded in separating two new metals from platinum. He dissolved the crude metal in aqua regia, evaporated off the excess acid and added a solution of mercurous cyanide, drop by drop, until a yellow precipitate appeared. When this substance was washed and ignited, a white metal remained. By heating the yellow precipitate with sulfur and borax he also succeeded in obtaining a button of the new metal, which he named *palladium* in honor of the recently discovered asteroid, *Pallas* (*6*).



From Berzelius' "Lehrbuch der Chemie"

BELLOWS USED WITH SEFSTRÖM'S FORGE

The first knowledge that the London public received of this discovery was an anonymous handbill offering the metal for sale. The humorous and pathetic story of the young Irish chemist, Richard Chenevix (*8*), who believed the new metal to be fraudulent and who tried to prove that it was a platinum amalgam, has been told by White and Friedman in the JOURNAL OF CHEMICAL EDUCATION (*21*).

In 1809–10 Joseph Cloud, chemical director of the Philadelphia Mint, discovered an alloy of gold and palladium in two ingots of gold from Brazil (*48*), (*49*). Although this alloy contained no easily oxidizable metal, silver, nor platinum, he obtained from it a button of palladium. Since palladium had previously been obtained only from impure platinum, some chemists may still have believed with Richard Chenevix that it must be an alloy of platinum. Cloud's isolation from the platinum-free ingots of a metal which proved to be identical with Dr. Wollaston's palladium afforded strong evidence that the latter must be an individual metal and not an alloy of platinum (*50*).

When the gold bars from Gongo-Soco, Brazil, first began to come to England, the Mint refused to accept them because of their brittleness. The famous platinum refiner Percival Norton Johnson assayed them, however, detected the palladium, and perfected a process for refining and toughening the Brazilian gold (*51*), (*52*). In 1837 he presented specimens of palladium-gold, palladium ammonium chloride, and palladium metal to W. A. Lampadius of the Freiberg School of Mines. According to Lampadius, "Palladium has not been separated from the Brazilian gold until the last four years, but since that time Mr. Johnson, who had worked on palladium a great deal with the late Wollaston, has given the owners of the aforementioned gold mine a method of parting by means of which the gold is produced pure, and the separated palladium put to many other uses .... The palladium thus produced, alloyed with 20 per cent silver, is now used in London as metal for dentists, also for making scales for sextants and other astronomical instruments. Alloyed with copper, it gives a composition which makes steel more elastic. Even earlier, a watchmaker, Bennet, specified an alloy of 24 palladium, 44 silver, 72 gold, and 92 copper for bearings for chronometers" (*52*).

Johnson separated the palladium from an enormous quantity of the Gongo-Soco gold, and in 1845 supplied the Royal Geological Society of London with a sufficient quantity of this metal for the casting of the Wollaston Medal (*44*). Johnson was always considerate of the miners, and sincerely devoted to their welfare. He spent much of his time and fortune on the schools which he erected near the mines (*51*).

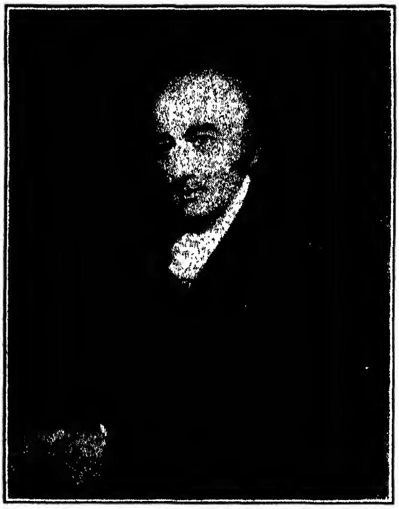
Rhodium

Dr. Wollaston dissolved another 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 mercurous cyanide to precipitate the palladium as palladious cyanide. After filtering off the precipitate, he decomposed the excess mercurous cyanide in the filtrate by adding hydrochloric acid 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 a new metal (*3*), which, because of the rose color of its salts, Dr. Wollaston named ***rhodium*** (*9*). 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.

Thomas Thomson relates that Dr. Wollaston had amazingly keen vision and remarkably steady hands. He could write on glass with a diamond in clear, well-formed letters which were so small that other persons could read them only with a microscope (*4*).

That Berzelius was well acquainted with Dr. Wollaston and held him in high esteem may be seen from his letter to Berthollet written in London in October, 1812:

> My stay here [said Berzelius] has been most interesting and instructive in furnishing me a quantity of chemical resources of which I formerly had no idea. But what I value most of all is the personal acquaintance of the admirable Wollaston and the brilliant Davy. I am sure that among the chemists who are at present in the prime of life there is none that can be compared with Wollaston in mental depth and accuracy as well as in resourcefulness, and all this is combined in him with gentle manners and true modesty. I have profited more by an hour's conversation with him than frequently by the reading of large printed volumes. . . . Simplicity, clarity, and the greatest appearance of truth are always the accompaniments of his reasoning (*5*).



WILLIAM HYDE WOLLASTON
1766–1828

English chemist and physicist. Discoverer of palladium and rhodium. Inventor of a process for making platinum malleable. Famous for his researches on force of percussion, gout, diabetes, columbium, tantalum, and titanium, and his scale of chemical equivalents.

In the diary which he kept on this visit to England, Berzelius wrote,

> Dr. Wollaston, Secretary of the Royal Society, known through his numerous discoveries in chemistry and physics, is a man between forty and fifty years old, of very pleasant appearance, very polished manners, plainness and clearness in his conversation, interest in his slightest gesture, and with such a spirit of justice and gifted with such moderation in his views that it has become a common proverb that whoever argues with Wollaston is wrong (*30*).

The letters of Dr. Marcet to Berzelius give us a pleasing picture of Dr. Wollaston's friendly nature. On May 24, 1814, Dr. Marcet wrote:

> Would you believe it, my dear friend, that while your kind and interesting letter of April 12th was on its way to London, I was occupied with friend Wollaston in enjoying all the dissipations of Paris. One fine morning, near the end of April, Wollaston came into my house

and said to me: "I have curious news for you." "What!" I replied, "Has Bonaparte returned to Paris?" "No," he said, "it is even more curious than that.... I am going to Paris tomorrow, and you are one of the party." I rubbed my eyes, thinking I was dreaming; but he finally proved to me that it was not a dream; and as everything Wollaston says is gospel (Sir John Sebright has nicknamed him "The Pope"), I immediately told my wife that fate was calling me to Paris for a fortnight, gave a good dose to each of my patients, and left....(*10*).

Sir Edward Thorpe gives quite a different picture of Wollaston, however, when he says,

> He resembled Cavendish in temperament and mental habitudes, and, like him, was distinguished for the range and exactitude of his scientific knowledge, his habitual caution, and his cold and reserved disposition (*11*).

On another occasion Dr. Marcet wrote, "The excellent Wollaston has just lost his father, who leaves a large fortune, which I dare to reply, will not spoil our friend" (*12*). On January 23, 1816, he suggested in reply to a question asked by Berzelius,

From Figuier's "Vies des Savants Illustres"

GEORGES-LOUIS LECLERC, COMTE DE BUFFON, 1707–1788

French naturalist famous for his beautiful literary style. Founder of the Jardin des Plantes. Author of a "Natural History" in forty-four volumes, in which he discussed insects, birds, quadrupeds, minerals, the theory of the earth, and the epochs of Nature. One of the first to investigate platinum.

> If you wish to send Wollaston a present in the name of the prince, the only idea that comes to me is a fine hunting gun of your splendid Swedish steel. The dear Doctor, pope that he is, has taken seriously to

> hunting, and already acquits himself with much success. The fact is he does not know how to do anything poorly (*10*).

Dr. Wollaston was a man of very broad interests, as a list of his publications will show. His papers were on such diverse subjects as: force of percussion, fairy rings, gout, diabetes, seasickness, metallic titanium, the identity of columbium and tantalum, a reflection goniometer, micrometers, barometers, a scale of chemical equivalents, and the finite extent of the atmosphere. He died in London on December 22, 1828 (*13*).

Osmium and Iridium

Smithson Tennant, the discoverer of osmium and iridium, like Dr. Wollaston, was the son of a clergyman. He was born in Wensleydale, near Richmond, Yorkshire, on November 30, 1761. At the age of nine years he had the misfortune to lose his father, and not many years later he witnessed the tragic death of his mother, who, while riding with him, was thrown from her horse and instantly killed. Tennant's elementary education was fragmentary, but even when very young he was fond of reading chemical books and performing experiments. When he was only nine years old he made some gunpowder for fireworks (*14*).

In 1781 he went to Edinburgh to study under the famous chemist and physician Dr. Black, and in the following year he entered Christ's College, Cambridge, where he studied chemistry, botany, mathematics, and Newton's "Principia." His room at college was a scene of confusion: books, papers, and chemical apparatus littered the floor, and his indolent and unsystematic habits were indeed a serious handicap throughout his scientific career (*15*).

When he was twenty-three years old, he traveled through Denmark and Sweden, where he met the famous Scheele, and for the rest of his life he delighted in showing his English friends the minerals that the great Swedish chemist had given him on this occasion. Tennant also traveled through France and the Netherlands and met the most eminent chemists of those countries. Berzelius said that Tennant always carried in his pocket a map of Sweden which had become worn and soiled through years of use and that he spoke French "gladly and well" (*30*). He received his degree of Doctor of Medicine from Cambridge in 1796, but never practiced.

In the same year he proved by an ingenious experiment that the diamond consists solely of carbon. This he did by burning a weighed diamond by heating it with saltpeter in a gold tube. The carbon dioxide united with the potash in the saltpeter, and was later evolved. Most chemists would have felt deep concern over the outcome of such a costly and important experiment, but Tennant went horseback riding at his usual hour, leaving the results to the mercy of his assistant. However, since the assistant was no other than the gifted William Hyde Wollaston, the outcome was successful (*14*), (*16*).

In 1803 Tennant found that when crude platinum is dissolved in dilute aqua regia, there remains a black powder with a metallic luster. This had been observed before and was thought to be graphite, but Tennant investigated it carefully in an attempt to alloy lead with it, and concluded that it contained a new metal (*17*). In the autumn of the same year Collet-Descotils, a friend and pupil of Vauquelin, found that this powder contains a metal which gives a red color to the precipitate from an ammoniacal platinum solution (*18*). When Vauquelin treated the powder with alkali he obtained a volatile oxide which he believed to be that of the same metal with which Descotils was dealing (*19*).

In the meantime Tennant continued his researches, and the results which he communicated to the Royal Academy in the spring of 1804 showed that the powder contains two new metals, which may be separated by the alternate action of acid and alkali. One of these he named *iridium* because its salts are of varied colors, and the other one he called *osmium* because of its odor (*20*).

These discoveries may best be described in his own words:

> Upon making some experiments, last summer, on the black powder which remains after the solution of platina, I observed that it did not, as was generally believed, consist chiefly of plumbago, but contained some unknown metallic ingredients. Intending to repeat my experiments with more attention during the winter, I mentioned the result of them to Sir Joseph Banks, together with my intention of communicating to the Royal Society my examination of this substance, as soon as it should appear in any degree satisfactory.
>
> Two memoirs were afterward published in France [continued Tennant] one of them by M. Descotils and the other by Messrs. Vauquelin and Fourcroy. M. Descotils chiefly directs his attention to the effects produced by this substance on the solutions of platina. He remarks that a small portion of it is always taken up by nitromuriatic acid during its action on platina; and, principally from the observations he is thence enabled to make, he infers that it contains a new metal, which, among other properties, has that of giving a deep red colour to the precipitates of platina. M. Vauquelin attempted a more direct analysis of the substance, and obtained from it the same metal as that discovered by M. Descotils. But neither of these chemists have observed that it contains also another metal, different from any hitherto known. . . .

Tennant gave the name iridium to the metal which Descotils and Vauquelin had observed, and the name osmium to the new one (*20*). In speaking of iridium, osmium, palladium, and rhodium, W. T. Brande stated in his lectures in 1817, "Of these, the two former were discovered by the late Mr. Tennant and the two latter by Dr. Wollaston; and had we searched throughout chemistry for an illustrative instance of the delicacy of the modern art of analysis, it would be difficult to have found any one more notorious than the history of the discovery and separation of these bodies exhibits" (*46*). During the entire course of the researches which led to the discovery of these four metals, Dr. Wollaston and Tennant had friendly intercourse with each other, and each kept in close touch with the other's work. As a brief relaxation from their scientific labors, they visited the Giants' Causeway together.

Smithson Tennant had a most kind and forgiving nature. When a dishonest steward on his estate, who had become so heavily in debt that Tennant was obliged to examine the accounts, committed suicide, Tennant not only excused the unfortunate family from the payment of the debt, but assisted them financially in the kindest possible manner (*14*).

Tennant, like Wollaston, enjoyed the esteem and friendship of the great Swedish master, Berzelius, who paid him a visit in the summer of 1812. Together they rode on horseback to inspect the 100-acre experimental oat field in which Tennant had mixed lime with the soil in decreasing ratio from one end to the other (*31*). After he had shown Berzelius the tall, well-developed oats at the highly limed end and the sickly plants at the other end of the field, they visited the lime-kiln which Tennant himself had designed (*30*).

Berzelius may perhaps have envied the English chemist's horsemanship, for, after receiving the Cross of the Order of the Northern Star, he said in a letter to Dr. Marcet, "Here I am then a kind of cavalier, I whose manner of mounting a horse Tennant can describe to you"* (*24*). In a letter to J. G. Gahn, Berzelius wrote: "Tennant is of about the same age as Wollaston, but is gray-haired and looks like an old man. He is a charming man, gets off a lot of droll ideas which entertain any sort of society, scientific or otherwise. He is a rather good, reliable chemist, but doesn't have either Wollaston's or Davy's head; and now he has lost much of his memory, so that one can tell him the same thing on two successive days with full assurance that it will be new to him. He is badly dressed, is careless of his appearance, and makes a poor showing. His chemicals are so helter skelter that he gets permission to pull out all the table drawers in the parlor to convince himself of the absence of what one would never expect to find except in a laboratory" (*53*)

In May, 1813, Dr. Marcet wrote to Berzelius, "Our friend Tennant has just been elected professor of chemistry at Cambridge after a very long struggle with a candidate who had many friends. His position demands that he give twenty lectures a year, which will not be very difficult for him (*22*). Berzelius replied, "Congratulate Tennant for me on his new profes-

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* "Me voilà donc une espèce de chevalier, moi, dont Tennant peut vous apprendre comment je monte à cheval."

sion and tell him that we expect from his hands the life of Newton more correct than we have yet seen it" (*23*).

Tennant was destined to give his lecture course at Cambridge only once, for his life was cut short by a tragic accident, the following account of which was written by Dr. Marcet to Berzelius on March 29, 1815:

> You have doubtless learned of the tragic death of poor Tennant. I was often on the point of writing you, but the grief of being the first to tell you this story restrained me. He had spent six months in France and was returning loaded with curious observations in geology, chemistry, political economy, etc. He had, it is said, discovered in sea water the source and origin of iodine. He announced himself every week for a month or so, and nevertheless did not come. Quite like himself, he clung to all the objects along the way, and advanced only very slowly. He finally arrives at Calais, then at Boulogne, and after having spent about fifteen days between these two places while waiting for a perfectly favorable wind, he finally sets sail. But a calm arises and they are obliged to return to port. Our friend seeks to console himself for this disappointment by taking a horseback ride; he proposes to a Prussian officer who was on board with him that they go together to see a column erected to Bonaparte a few miles from Boulogne.
>
> They had to pass over a little draw-bridge [continued Dr. Marcet]. The officer goes over first, but as soon as he is on the bridge he notices it pivoting on its center and that it is going to open into the ditch. He cries to Tennant, "Don't come any farther," and at the same time rushes on to re-establish equilibrium, but it was too late; he feels that another force is pressing on the bridge and forcing it to an inclined plane. . . he slides back with his horse and falls from twelve to fifteen feet into the ditch. Recovered from his shock, he looks around him and sees poor Tennant lying against the wall at the end of the ditch with his horse writhing on top of him. He pushes the horse away, lifts our friend, and finds him dying. . . . Who would have thought that our friend would die while visiting a work of war, of which you know he had the greatest horror. You well know, and I have no need to tell you, all that his friends, all that science, have lost. He was a unique man and one who will probably never be replaced. He loved you dearly, and I know you will mourn him sincerely (*24*).

Tennant had "an expressive, intelligent face. . . an intuitive and prompt perception of truth. . . a broad mind, deep moral feelings, and a zeal for the improvement of mankind" (*15*). He delighted in the artistic achievements of Virgil, Milton, Pascal, Gray, Handel, and Raphael. His neverfailing sense of humor consisted in "fanciful trains of imagery, in natural, but ingenious and unexpected, turns of thought and expression, and in amusing anecdotes, slightly tinged with the ludicrous. The effect of these was heightened by a perfect gravity of countenance, a quiet, familiar manner, and a characteristic beauty and simplicity of language" (*15*).

Ruthenium

The element ruthenium is the little Benjamin of the platinum family. It did not see the light until more than a century after the discovery of platinum, but, to avoid separating it too far from its older brothers, its story will be told here.

In 1828 Berzelius and G. W. Osann (*25*), professor of chemistry at the University of Dorpat, Russia, examined the residues left after dissolving crude platinum from the Ural mountains in aqua regia. Berzelius did not find in them any unusual metals except palladium, rhodium, osmium, and iridium, which had already been found by Wollaston and Tennant in similar residues from American platinum. Professor Osann, on the other hand, thought that he had found three new metals, which he named pluranium, ruthenium, and polinium (*25*), (*36*). In 1844, however, Professor Klaus, another Russian chemist, showed that Osann's ruthenium oxide was very impure, but that it did contain a small amount of a new metal (*26*), (*33*).

Courtesy Mr. W. D. Trow

KARL KARLOVICH KLAUS, 1796–1864

Professor of pharmacy and chemistry at the Universities of Dorpat and Kazan. He was a great authority on the chemistry of the platinum metals.

Karl Karlovich Klaus* spent his infancy and boyhood in a harsh, unkind environment.† He was born in the Baltic-Russian city of Dorpat§ on January 23, 1796. His father, a talented painter whose pictures later adorned Klaus's library, died in 1800. Soon after her husband's death the mother married another artist, and she, in turn, died when the boy was only five years old. Her second husband soon married again, and thus the little boy found himself a strange child in a strange home, left without affection and almost without care (*36*).

Klaus soon showed ability in design and sculpture, and his love for art, poetry, and drama helped him at times to forget the none-too-gentle home

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* The name is frequently written Carl Ernst Claus. It is a German name, not a Russian one.

† Most of the details regarding the life of Klaus would have been inaccessible without the kind assistance of Mr. M. K. Elias of the Kansas State Geological Survey, who translated Menschutkin's biographical sketch from the Russian. The author is sincerely grateful to him.

§ This city is located in Esthonia, and is now known as Tartu.

surroundings. He attended the grade school and gymnasium in Dorpat, but was unable, in spite of his excellent record, to complete the course at the latter institution. However, the praise given by his teachers stimulated him to further efforts which, even at this early age, revealed the fundamental features of his character: resoluteness, optimism, and a desire to reach at any cost a once-attempted goal. As a boy he enjoyed the few bright aspects of his cheerless life, and as an adult he never complained of the sufferings of his childhood.

When forced to earn his own living at the age of fourteen years, he became an apprentice in a pharmacy in St. Petersburg. Here he spent his spare moments reading books on chemistry, pharmacy, and allied sciences. These attempts at self-education were so successful that Klaus was soon able to pass the examinations, first for assistant pharmacist and then for the position of provisor (*36*).

In 1815 he went back to Dorpat, passed the pharmacy examinations at the University, and returned to the St. Petersburg apothecary. His study of the natural sciences having awakened in him a desire to study Nature at first hand, he went to Saratov in 1817 as provisor of a pharmacy so that he might spend his leisure hours investigating the flora and fauna of the Volga steppes, or prairies, in eastern Russia. The results of this ten-year research were published in the Russian journals.

After his marriage in 1821 Klaus longed to have an apothecary shop of his own, and five years later he began business in Kazan, where he soon had the best pharmacy in the town. Here, with more adequate financial resources, he continued his study of the flora and fauna. He soon became recognized as an authority on that subject, and his advice was sought whenever a scientific expedition was to be sent into the steppes. This brought him into contact with many famous scientists, who always carried away a pleasant recollection of his modesty and willingness to coöperate. The expedition which he himself made in 1827 through the region between the Urals and the Volga afforded material for his large book entitled "Volga Flora" (*36*).

When an assistantship in the chemistry department of the University of Dorpat was offered to him in 1831, Klaus sold his store at a loss, made the long trip back to Esthonia, and accepted the modest position, in order to devote all his time to scientific research. While completing the work for his master's degree in chemistry, he found time to explore with Göbel and A. Bergmann the Trans-Volga salt marshes and to prepare all the sketches for a large, two-volume record of the expedition, which was published at Dorpat in 1837 and 1838. In recognition of this work he was awarded the Demidoff prize.

Wishing to return to Kazan, he applied to the Secretary of Public Instruction for a position at the University. The Secretary approved the application, but only after listening to a trial lecture which Klaus was required to deliver at the Medico-Surgical Academy of St. Petersburg (*36*).

Upon returning to Kazan as adjunct in chemistry, he entered enthusiastically into the work of remodeling the old chemical museum into a chemical laboratory. Klaus also succeeded in getting six additional rooms in a newly completed university building. These were arranged like Liebig's laboratory at Giessen, and included a large lecture room, well equipped for demonstration experiments. He was granted an appropriation of about 10,000 rubles ($5000) for the purchase of glassware, reagents, and apparatus.

In 1838 Klaus, with his student assistant Kabalerov, made an analysis of the water from the Sergievsky Mineral Springs, which provided the data for his dissertation for the doctorate in pharmacy. Immediately after receiving this degree, he was made extraordinary professor at the University, and six years later he was promoted to the position of ordinary professor.

In 1840 Klaus became interested in platinum residues. The reader will recall that in 1828 Professor G. W. Osann of Dorpat University had announced the presence in these residues of three new metals, the existence of which Berzelius had denied. Professor Klaus wished to settle this question, and the first step in his investigation was a careful repetition of Osann's work. He obtained two pounds of platinum residues from P. G. Sobolevsky, a platinum refiner in St. Petersburg, and was surprised to find that they contained 10% of platinum, besides smaller amounts of osmium, iridium, palladium, and rhodium. In his report one may read,

> The unexpected richness of the residues, great quantities of which lie unused at the laboratory of the Government Mint at St. Petersburg, appeared to me so important that I immediately reported the results of my investigation to the government mining authorities, and in 1842 I went to the capitol (*36*).

In St. Petersburg he interviewed Count Egar F. Kankrin, the Secretary of the Treasury who introduced platinum coinage in Russia. Kankrin expressed complete approval of Professor Klaus's investigation, and Chevkin, the chief of the staff of mining engineers, presented him with twenty pounds of the platinum residues.

The working of these residues did not prove as profitable as Professor Klaus had hoped, for, as he said:

> These residues were poorer than the first, and thus my hope of adapting my method for profitable extraction of platinum from them was not fulfilled. There remained only an investigation interesting for science. Since I came to realize this two years ago, I have worked constantly on this hard, prolonged, and even unhealthful investigation; now I report to the scientific world the results obtained: (1)

> results of analysis of rich residues; (2) new methods for the separation of the metals of the platinum group; (3) methods for working up poor residues; (4) discovery of a new metal, ruthenium; (5) results of the analysis of poor residues and the simplest methods of decomposition of platinum ores and residues; (6) new properties and compounds of the previously known metals of the platinum group. All this may serve as a contribution to the chemical history of the precious metals of our fatherland (*36*).

Klaus obtained the new metal from osmiridium, the portion of the crude platinum which is insoluble in aqua regia. He calcined a mixture of osmiridium, potash, and potassium nitrate in a silver crucible placed inside a Hessian crucible on a layer of magnesia (*27*). After heating it for an hour and a half at bright redness, he poured the molten contents into an iron capsule. He then took up the melt in a very large volume of water, and allowed it to stand four days in the dark in a completely filled bottle.

The orange-colored solution, containing, among other things, potassium ruthenate, was treated with nitric acid, whereupon a black precipitate of osmium dioxide containing from fifteen to twenty per cent of ruthenium oxide was thrown down as a velvety deposit. Klaus distilled this with aqua regia, taking care to condense the osmium tetroxide. The residue remaining after the distillation consisted mainly of the sesquichloride and tetrachloride of ruthenium. By adding ammonium chloride, Klaus prepared ammonium chlororuthenate, $(NH_4)_2RuCl_6$, a salt which upon calcination yields spongy ruthenium (*27*), (*38*).

This report, which was entitled "Chemical investigation of the residues of ural platinum ore and of the metal ruthenium," occupied one hundred and eighty-eight pages in the *Scientific Annals of Kazan University* for 1844. In the following year it was published in book form. For patriotic reasons and also in recognition of the earlier work of Professor Osann, Klaus retained the name *ruthenium*, which means *Russia*. The white substance which Osann had taken for the oxide of this new metal consisted chiefly of silicic and titanic acids, iron peroxide, and zirconia. The new metal had escaped him because he had repeatedly treated this insoluble material with hydrochloric acid without examining the solution (*37*).

When Professor Klaus sent a sample of the new metal to Berzelius, the great Swedish master was skeptical. On January 21, 1845, he remarked in a letter to Wöhler:

> Probably Klaus's experiments on the residues from platinum ores and on the new metal ruthenium have already been described in the German journals. He sent me his paper in manuscript. You see thereby that he has also prepared colorless salts of iridium with sulfurous acid The early severe winter in November interrupted the

> postal communication between Ystad and Stralsund, so that I have not received the German journals for three months (*28*).

In the meantime Klaus continued his investigation of the compounds of ruthenium, specimens of which he sent to Stockholm, one after another, with detailed descriptions of their properties and the methods of preparation. This evidence was so convincing that in 1845 Berzelius announced in the *Jahresbericht* his acceptance of ruthenium as a new element (*36*), (*37*).

On March 9, 1846, he again mentioned Klaus's paper to Wöhler, saying:

> Klaus in Kazan has sent me a résumé (*Nachernte*) concerning ruthenium, which I expect to read tomorrow at the Academy and which you shall then receive in the Öfversigten. It is strange that he does not publish his longer paper. A copy of it has been in my hands since November, 1844. Yet he surely cannot have intended that I should publish it. At least he has never said a word about it. . . .

J. HENRI DEBRAY
1827–1888

French chemist who collaborated with Henri Sainte-Claire Deville at the École Normale Supérieure in researches on gaseous dissociation. He also investigated beryllium, molybdenum, tungsten, and the metals of the platinum group, and made contributions to synthetic mineralogy. It was in Debray's laboratory that Moissan liberated fluorine.

Berzelius finally suggested to Klaus that he send the ruthenium paper to Wöhler for publication in the *Annalen*, and it may now be seen in Volume 63 of that journal (*29*), (*38*).

All of Klaus's papers on the platinum metals were collected and published in 1854 in a Jubilee Volume issued in honor of the fiftieth anniversary of the founding of the University of Kazan. He continued to teach inorganic, analytical, and organic chemistry, and was assisted for a time in the organic course by Nikolai Nikolayevich Zinin and in the inorganic course by Alexander Michaylovich Butlerov.

In 1852 Klaus was invited to occupy the chair of pharmacy at the University of Dorpat and to take charge of the Pharmaceutic Institute, at that time the only institution of its kind in all Russia. He accepted the appointment, left his position at Kazan in charge of Butlerov, abandoned the long-cherished steppes of the Volga, and made the long trip back to Esthonia.

At Dorpat he continued his investigation of the platinum metals and their alloys. After devoting twenty years to research in this field, he wished to publish a monograph which should include not only his own researches but those of other scientists. In 1863 the Russian government sent him to western Europe to visit the laboratories and platinum refineries and to study the history of the platinum metals in the libraries of the great scientific centers. Klaus's achievements were so well known that he was honored wherever he went. In Berlin he met Heinrich and Gustav Rose, Poggendorff, and Magnus, and in Paris he studied the electric furnaces of Henri Sainte-Claire Deville and H. Debray (*36*).

Professor Klaus returned to Dorpat in January, 1864, with a wealth of material for the monograph on the platinum group, but illness unfortunately overtook him, and the work was never completed. He passed away on March 24, 1864, loved and respected by his students and colleagues.* In his last public address before the Pharmaceutical Society of St. Petersburg, he emphasized the desirability of providing scholarships for needy students (*36*).

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XV. THREE ALKALI METALS: POTASSIUM, SODIUM, AND LITHIUM

A number of the chemical elements, including some that play an important rôle in modern life, remained practically unknown outside the scientific world for many years after their discovery. Some, like tellurium, vanadium, and titanium, were forgotten for several decades even by chemists, and were later rediscovered. The reader will recall, however, that when phosphorus was discovered in 1669 the news spread rapidly throughout Europe. In a similar manner Davy's isolation of sodium and potassium immediately fired the imagination of the nineteenth-century public and aroused intense interest. These elements, like phosphorus, made their entrance upon the chemical stage in a manner nothing short of dramatic, and the accompanying phenomenon of light helped to focus all eyes upon them. Lithium, however, entered the chemical world in a more quiet manner and was introduced by a scientist of lesser prominence, J. A. Arfwedson, a student of Berzelius.

. . . .

> *There is now before us a boundless prospect of novelty in science; a country unexplored, but noble and fertile in aspect; a land of promise in philosophy (1).*

Potassium and Sodium

Ancient writers did not distinguish between sodium carbonate (the mineral alkali) and potassium carbonate (the vegetable alkali) (*42*). When Johann Bohn prepared aqua regia in 1683 by distilling a mixture of salt and aqua fortis (nitric acid), he noticed that the cubic crystals which remained differed from those of saltpeter prepared in the ordinary manner from wood ashes. This clear distinction between "cubic saltpeter" (sodium nitrate) and ordinary saltpeter was an important step in the proof that soda and potash are two different alkalies. In the latter part of the eighteenth century, Torbern Bergman wrote: "There are to this day persons who insist that the vegetable alkali cannot be exhibited in form of crystals, notwithstanding that Professor Bohnius (*Diss. Physico Chym., ann.* 1696, pa. 381) of Leipsic, so long ago as the end of the last century, had demonstrated the contrary; but his method had been so long unknown that it was lately offered to the public as a new discovery" (*42*), (*43*), (*44*).

In speaking of the loss to both chemistry and medicine by too narrow specialization in either science, Hermann Boerhaave once wrote, "What praise then is not merited by Jean Bohn and Frederic Hoffmann, who excel in both and who thereby acquired such a great reputation" (*45*).

George Ernst Stahl distinguished between the "natural and artificial alkalies" (soda and potash) as early as 1702, and noted that certain sodium salts differ in crystalline form from those of potassium (*42*). Hermann Kopp quoted a passage from the "Specimen Becherianum" in which Stahl stated that the natural alkali (soda) in common salt appeared in the retort after distillation with concentrated oil of vitriol or spirit of niter (sulfuric or nitric acid) in the form of new salts differing from the corresponding salts of the artificial alkali (potash) in their crystalline form, solubility in water, and behavior toward heat.

Henri-Louis du Hamel du Monceau (or Dumonceau) proved conclusively in 1736 that the mineral alkali (soda) is a constituent of common salt, of Glauber's salt, and of borax. He was born in Paris in 1700 and educated at Harcourt College. Even before his election to membership, the Academy of Sciences selected him to study a disease which was threatening the saffron crop in Gâtinois. Du Hamel found the cause of it to be a parasitic plant, and decided to devote his life to scientific agriculture and the public welfare (*50*).

Gal. franç., 1823.
Drouais père pinx., H. Grevedon del.

HENRI-LOUIS DU HAMEL
(*or* DUHAMEL) DU MONCEAU
1700–1782

French chemist and agriculturist who proved in 1736 that the mineral alkali (soda) is a constituent of common salt, of Glauber's salt, and of borax. With his brother, M. de Denainvilliers, he carried out important experiments in plant nutrition on their estate.

Although the acidic constituent of common salt was already known, the nature of its basic constituent was still a matter of conjecture. "Soda, *natrum*, and borax," wrote du Hamel in 1736, "give with vitriolic acid Glauber's salt; with acid of saltpeter, cubic saltpeter [sodium nitrate]; and with acid of salt, a kind of sea salt. Does this not permit one to decide as to the base of the sea salt?" (*46*).

He prepared soda from salt by two methods. In the first of these, he evaporated a mixture of salt and oil of vitriol, heated the resulting Glauber's salt with charcoal dust in a closed crucible, distilled the reduced mixture with wine vinegar, and calcined the hard, black residue of sodium acetate left in the broken retort. In his other method, he poured concentrated spirit of saltpeter (nitric acid) on the salt, and distilled off the resulting aqua regia. After repeating the distillation four times, he exploded the residue of cubic saltpeter (sodium nitrate) with charcoal dust in a red-hot crucible. On dissolving the residue, he obtained "the crystalline salt of an alkali, as in the foregoing process" (*46*). He concluded that "soda is certainly nothing other than the true base of sea salt; this is shown by the habitat of soda plants" (*46*).

In an attempt to find out whether the presence of soda or potash depended on a specific difference in the plants which produce them or on the composition of the soils, du Hamel devoted many years to agricultural experiments, at his estate at Denainvilliers, on the culture of the common saltwort (*Salsola* kali), a plant used for the manufacture of soda ash. The final analyses of the ash of this plant proved that in the first year the mineral alkali still predominated, but that in succeeding years the vegetable alkali rapidly increased until finally, after a few generations, the soda had almost disappeared (*50*). In these experiments, he had for many years the invaluable and enthusiastic help of his brother, M. de Denainvilliers. In his eulogy of du Hamel in the History of the Academy of Sciences, the Marquis de Condorcet gave the following characterizations of the two brothers:

> While M. du Hamel wrote his books, consulted with scientists, kept up a correspondence with the most enlightened men in Europe, engaged in new scientific researches, and planned his experiments and observations, M. de Denainvilliers carried out, in his retreat, the observations and experiments which his brother had entrusted to him, always unknown and content to be so. . .asking no other recompense than the pleasure of having done good. To judge M. du Hamel, one would have to see him at Denainvilliers, the fields covered with exotic productions which were enriching growers whose fathers had not known even the names of these useful and salutary plants,. . . forests filled with exotic trees brought from all countries of the globe, . . .all the instruments invented for observing nature and studying her laws, distributed in the mansions, in the gardens, in the parks; and in the midst of all these objects of instruction, two men united by the love of the good, different in character as in occupation. . .(*50*).

In his books, M. du Hamel reported his own experiments and their results, and also included much elementary information for the use of practical farmers. "At the age of fifty years," said Condorcet, "he was one of the best informed men in Europe in all the scientific branches with the applications of which he later occupied himself almost exclusively. . .and if he has often been justly cited to show what use scholars ought to make of their learning, one can also prove by his example that, in order rightfully to aspire to the honor of making the sciences useful, one must be very learned" (*50*). M. du Hamel "kept all his life the principles of religion he had received in his childhood;. . .to serve humankind, to penetrate nature's marvels, and to ascribe them to their Author, seemed to him, for a scientist and citizen, the most fitting exercise of piety" (*50*). He lived tranquilly with his nephews, one of whom shared his scientific labors. After the death of M. de Denainvilliers, these nephews and a niece relieved M. du Hamel of all domestic cares. He lived to be eighty-two years old.

Georg Brandt in 1746 prepared both crystalline and amorphous sodium carbonate and observed that the latter is not hygroscopic and that it crystallizes more readily than does potassium carbonate (*47*).

In 1758–59 A. S. Marggraf prepared very pure cubic saltpeter from common salt. "After cooling the vessel and breaking the retort," said he, "I found in it a saline substance which took fire on glowing charcoal, without the slightest crackling (just as ordinary saltpeter does when very pure) and, as the chemists say, detonated, but with the difference that the flame was yellow; for that with ordinary prismatic niter is usually whitish" (*48*). In his next paper, which was entitled "Proof that the alkaline part separated from common salt is a true alkaline salt and not an alkaline earth," he mentioned the yellow flash of gunpowder made with cubic saltpeter and the blue (violet) flash of that made with prismatic saltpeter (*48*).

Although chemists had long suspected that the alkaline earths are metallic oxides, the true nature of soda and potash was not surmised before the early nineteenth century (*28*). Lavoisier believed that they might contain nitrogen:

> Up to the present [said he] the principal constituents of soda are no better known than those of potash. We are not even certain whether or not that substance is already formed in vegetables before combustion. Analogy might lead us to believe that nitrogen is one of the principal constituents of alkalies in general, and we have the proof of it in the case of ammonia, as I shall explain; but as far as potash and soda are concerned, we have only slight presumptions, not yet confirmed by any decisive experiment (*29*).

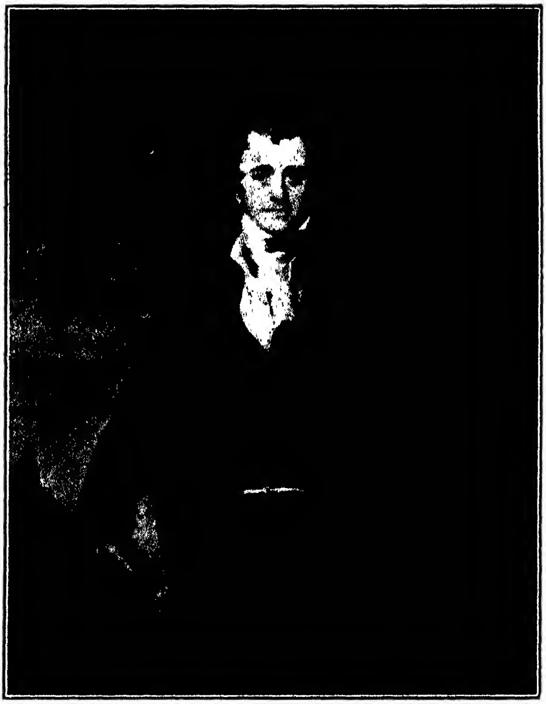
In his list of elements Lavoisier mentioned thirty-three substances:

light
caloric
oxygen
nitrogen
hydrogen
sulfur
phosphorus
carbon
muriatic radical
fluoric radical
boric radical
antimony
silver
arsenic
bismuth
cobalt
copper
tin
iron
manganese
mercury
molybdenum
nickel
gold
platinum
lead
tungsten
zinc
lime
magnesia
baryta
alumina
silica

In commenting on this list he said, "I have not included in this table the fixed alkalies, such as potash and soda, because these substances are evidently compound, although however the nature of the principles which enter into their composition is still unknown" (*30*). The chemical nature of these common alkalies remained unknown until the beginning of the nineteenth century, when the brilliant young English chemist, Humphry Davy succeeded in decomposing both of them with his voltaic pile.

High above an azure bay on the rugged coast of Cornwall there rises lofty St. Michael's Mount, a gigantic rock surmounted by an ancient turreted castle. The nearby town of Penzance in Mount's Bay may suggest to lovers of light opera the adventurous pirates of Gilbert and Sullivan, but chemists revere it as the birthplace of Sir Humphry Davy, who once gave the following vivid picture of the scene so dear to him:

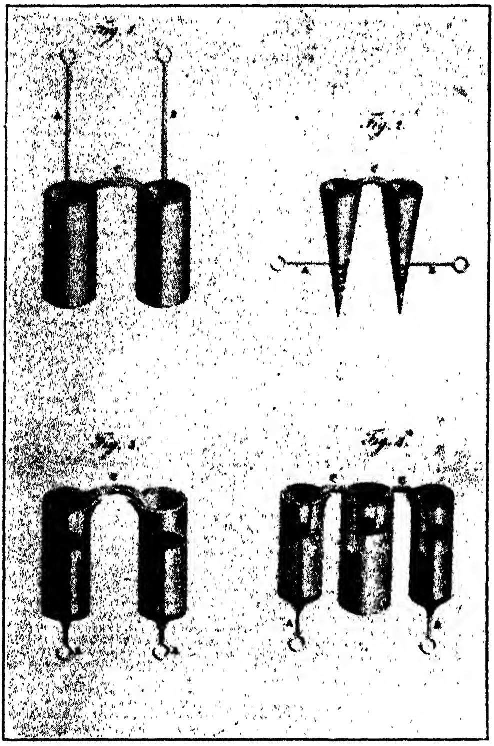
The sober eve with purple bright
Sheds o'er the hills her tranquil light
In many a lingering ray;
The radiance trembles on the deep,
Where rises rough thy rugged steep,
Old Michael, from the sea.
Around thy base, in azure pride,
Flows the silver-crested tide,
In gently winding waves;
The Zephyr creeps thy cliffs around,—
Thy cliffs, with whispering ivy crown'd,—
And murmurs in thy caves (*2*).



SIR HUMPHRY DAVY
1778–1829

English chemist and physicist. One of the founders of electrochemistry. Inventor of the safety lamp for miners. He was the first to isolate potassium, sodium, calcium, barium, strontium, and magnesium. Davy in England and Gay-Lussac and Thenard in France, working independently, were the first to isolate boron.

Humphry Davy was born on December 17, 1778. He was a healthy, active, affectionate child, who made many friends by his knack of telling stories and reciting original verses. His teacher, Dr. Cardew, said the boy's best work was done in translating the classics into English verse (*3*). Davy's schooling ended when he was only fifteen years old, but his education continued for the rest of his life. In 1795 he was apprenticed to Bingham Borlase, a surgeon and apothecary in Penzance, and two years later he began to study natural philosophy and chemistry (*20*). His textbook was Lavoisier's "Elements of Chemistry," his reagents were the mineral acids and the alkalies, and his apparatus consisted largely of wine glasses and tobacco pipes. When he was twenty years old Davy became superintendent of the Pneumatic Institution which Dr. Beddoes had recently established at Clifton for studying the medicinal value of gases. He was most happy in sharing the delightful home life of Dr. Beddoes and the social contacts with such distinguished literary men as Southey and Coleridge (*4*).



ELECTROCHEMICAL APPARATUS OF SIR HUMPHRY DAVY

Fig. 1. Agate cups.
Fig. 2. Gold cones.
Fig. 3. Glass tubes.
Fig. 4. The two glass tubes with the intermediate vessel.

In all the figures, *AB* denote the wires, one positive and one negative; and *C* the connecting pieces of moistened amianthus.

In 1801 Count Rumford obtained for Davy a position as assistant lecturer on chemistry and director of the laboratory at the Royal Institution. In the *Philosophical Magazine* one finds the following description of his first lecture, which was on galvanism:

> Sir Joseph Banks, Count Rumford and other distinguished philosophers were present. The audience was highly gratified, and testified their satisfaction by general applause. Mr. Davy, who appears to be very young, acquitted himself admirably well. From the sparkling intelligence of his eye, his animated manner, and the tout ensemble, we have no doubt of his attaining distinguished excellence (*5*).

Literary persons and the members of fashionable society, as well as scientists, flocked to his lectures. Davy kept a careful record of all his experiments and showed it willingly to all who were interested. He remained with the Royal Institution for eleven years, and then retired at the time of his marriage.

Humphry Davy's greatest successes were in the field of electrochemistry. In his first attempts to decompose the caustic alkalies, he used saturated aqueous solutions, but succeeded in decomposing nothing but the water.

On October 6, 1807, however, he changed his plan of attack. "The presence of water appearing thus to prevent any decomposition," said he, "I used potash in igneous fusion" (*22*), (*23*), (*26*).

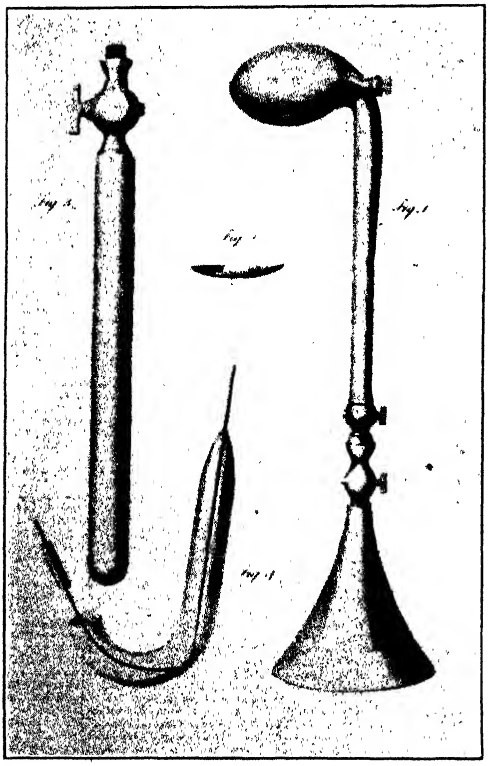
To his great surprise he noticed intense light at the negative pole and a column of flame rising from the point of contact. When he reversed the current the flame came always from the negative pole. Since perfectly dry potash is a non-conductor, Davy gave it a brief exposure to the air:

> A small piece of potash [said he], which had been exposed for a few seconds to the atmosphere so as to give conducting power to the surface, was placed upon an insulated disc of platina, connected with the negative side of the battery of the power of 250 of 6 and 4, in a state of intense activity; and a platina wire, communicating with the positive side, was brought in contact with the upper surface of the alkali. The whole apparatus was in the open atmosphere.
>
> Under these circumstances [said Davy] a vivid action was soon observed to take place. The potash began to fuse at both its points of electrization. There was a violent effervescence at the upper surface; at the lower, or negative, surface, there was no liberation of elastic fluid; but small globules having a high metallic lustre, and being precisely similar in visible characters to quicksilver, appeared, some of which burnt with explosion and bright flame, as soon as they were formed, and others remained, and were merely tarnished, and finally covered by a white film which formed on their surfaces.
>
> These globules, numerous experiments soon shewed to be the substance I was in search of, and a peculiar inflammable principle the basis of potash. I found that the platina was in no way connected with the result, except as the medium for exhibiting the electrical powers of decomposition; and a substance of the same kind was produced when pieces of copper, silver, gold, plumbago, or even charcoal were employed for compleating the circuit.

DR. THOMAS BEDDOES
1760–1808

English physician and chemist. Founder of the Pneumatic Institution at Clifton for studying the therapeutic value of gases. Sir Humphry Davy became the superintendent of this institution at the age of twenty years.

The little metallic globules always appeared at the cathode, and these had an astonishing way of bursting into flame when thrown into water. They skimmed about excitedly with a hissing sound, and soon burned with a lovely lavender light. Davy found that the new metal liberated hydrogen from the water and that the flame was caused by the burning of this gas (*6*), (*23*). Because he had obtained the metal from potash, he named it *potassium*. Dr. John Davy, who was present when potassium was isolated for the first time, said that his brother became greatly excited and almost delirious with joy (*7*), (*19*).



APPARATUS OF SIR HUMPHRY DAVY

Fig. 1. Retort of plate glass for heating potassium in gases.

Fig. 2. Platinum tray for receiving the potassium.

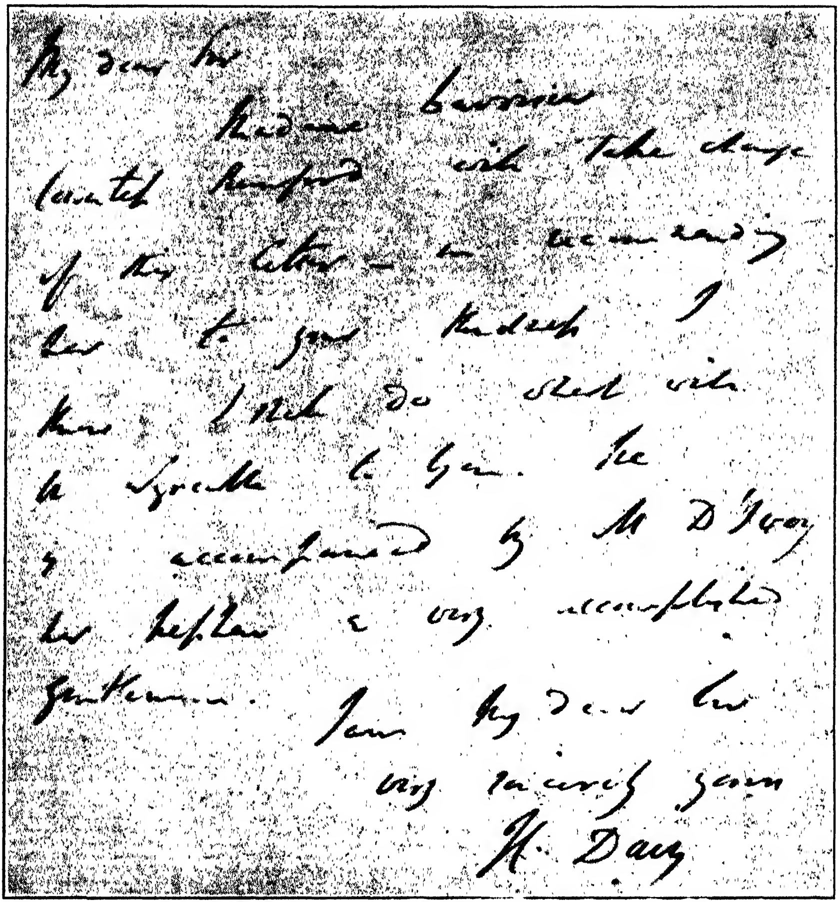
Fig. 3. Platinum tube for receiving the tray in distillation experiments.

Fig. 4. Apparatus for taking the voltaic spark in sulfur and phosphorus.

Humphry Davy then attempted to decompose caustic soda by a similar method, and found that a larger current was required (*6*), or, as he himself expressed it, that "the decomposition demanded greater intensity of action in the batteries, or the alkali was required to be in much thinner and smaller pieces:"

> With the battery of 100 of 6 inches in full activity [he explained] I obtained good results from pieces of potash weighing from 40 to 70 grains, and of a thickness which made the distance of the electrified metallic surfaces nearly a quarter of an inch; but with a similar power it was impossible to produce the effects of decomposition on pieces of soda of more than 15 or 20 grains in weight, and that only when the distance between the wires was about one-eighth or one-tenth of an inch. The substance produced from potash remained fluid at the temperature of the atmosphere at the time of its production; that from soda, which was fluid in the degree of heat of the alkali during its formation, became solid on cooling, and appeared having the lustre of silver (*23*), (*24*).

Thus only a few days after the discovery of potassium Davy was able to announce the isolation of another new metal, which he named *sodium*. However, it still remained for him to prove the elementary nature of these metals, which many chemists believed to be compounds of the alkali and hydrogen. Gay-Lussac and Thenard argued, for example, that, since ammonium = ammonia + hydrogen, potassium = potash + hydrogen. It was finally proved, however, that no hydrogen can be evolved from potassium, and that Davy was correct in regarding sodium and potassium as elements (*8*).



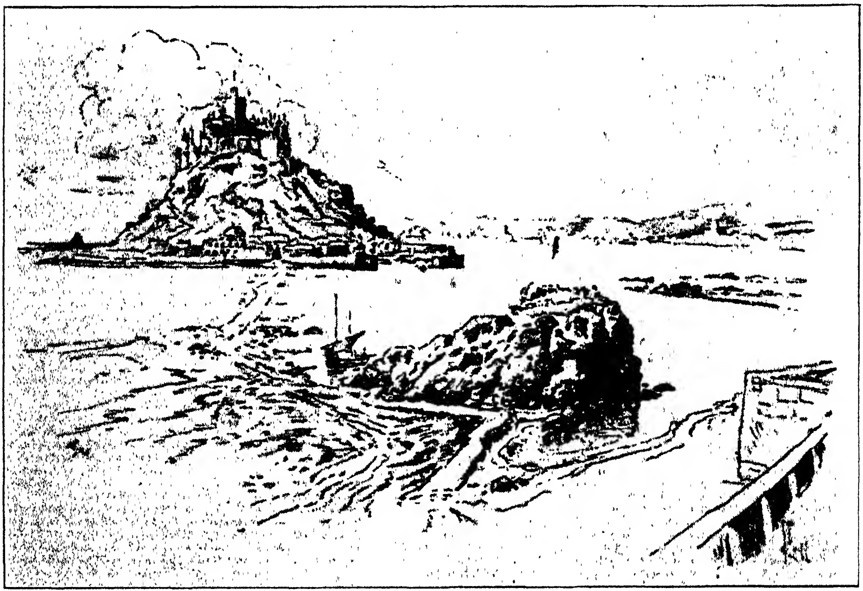
My dear Sir
Madame Lavoisier
Countess Rumford will take charge
of this letter — in recommending
her to your kindness I
know [illegible] do [illegible] with
her [illegible] to you. She
is accompanied by M D'Ivernois
her nephew a very accomplished
gentleman. I am my dear Sir
very sincerely yours
H. Davy

Edgar Fahs Smith Memorial Collection, University of Pennsylvania

A LETTER BY SIR HUMPHRY DAVY IN WHICH HE INTRODUCES MME. LAVOISIER DE RUMFORD TO DR. URE OF GLASGOW

Mr. A. Combes, one of Davy's admirers, communicated some interesting comments on this discovery to *Nicholson's Journal* (*27*):

> I attended his course of lectures of 1807 [said Mr. Combes] and in referring to my notes I find that he stated it as a fact, that all bodies of known composition attracted by the negative pole in the Voltaic circuit consisted principally of inflammable matter, and were naturally positive; and that it was probable therefore, that all bodies of unknown composition attracted by this pole, and which were naturally positive, might also contain inflammable matter. In his lectures in 1801,* he stated, that, in looking for *inflammable matter* after those ideas in the fixed alkalies, he had *discovered* it, and that he had likewise found what he had not expected, that it was metallic in its nature. In this instance sagacious conjecture and sound analogy were followed up by experimental research, and ended in a great discovery.



From A. H. Norway's "Highways and Byways in Devon and Cornwall"

ST. MICHAEL'S MOUNT AND BAY NEAR PENZANCE, CORNWALL, WHERE SIR HUMPHRY DAVY WAS BORN

Davy's isolation of the alkali metals was brilliant in every sense of the word. It soon led to the discovery of the alkaline earth metals by a similar electrochemical method; and the alkali metals themselves were destined to become powerful tools in the search for other elements.

Lithium†

At the close of the eighteenth century, the great Brazilian scientist and statesman Jozé Bonifácio de Andrada e Silva made a mineralogical journey

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* This date as given in *Nicholson's Journal* is obviously incorrect.

† See also Chapter XVI, pp. 287–9.

through Scandinavia (*41*). In a letter to Mine Surveyor Beyer of Schneeberg which was published in January, 1800, in *Scherer's Journal,* he described an infusible, laminated mineral which he called petalite, which dissolved in nitric acid very slowly and without effervescence, and another new mineral which he called spodumene (*34*).

N.-L. Vauquelin's analysis of spodumene, which the Abbé Haüy published in his *Traité de Minéralogie* in 1801, showed a loss of 9.5 per cent, which was never correctly interpreted until J. A. Arfwedson in 1818 discovered a new alkali metal, lithium, first in petalite, and soon after in spodumene and in lepidolite (*35*). Even before the discovery of lithium, Johann Nepomuk von Fuchs observed the red color which spodumene imparts to the flame; he afterward expressed chagrin because he had neglected to investigate the cause of this color (*36*). Vauquelin detected the presence of an alkali in a specimen of petalite obtained from the metallurgist E. T. Svedenstjerna, but mistook it for potash (*13*), (*37*). Wilhelm Hisinger also analyzed this mineral at least as early as January, 1818, and obtained preliminary results similar to those of Arfwedson (*38*). When the Reverend Edward Daniel Clarke of the University of Cambridge analyzed a specimen of it in the same year, his results showed a puzzling "loss" of 1.75 per cent, the reason for which became evident as soon as Arfwedson's analysis was published (*39*), (*40*).

Sisson, Gal. dos Brazileiros Illus., 186
A. Sisson, lith.

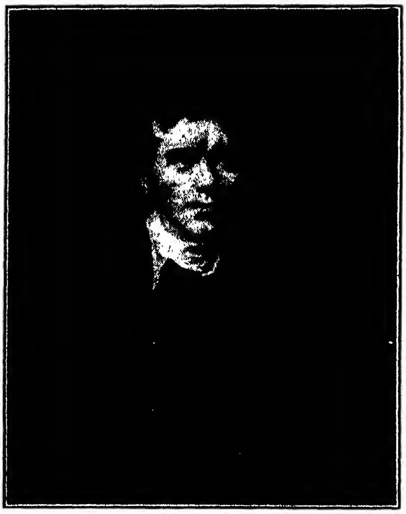
JOZÉ BONIFACIO DE ANDRADA E SILVA
1763-1838

Brazilian scientist, statesman, and poet. Discoverer of petalite and spodumene, minerals in which Arfwedson discovered lithium. He worked tirelessly to improve the social conditions of the dispossessed Indians and enslaved Negroes and to bring about their gradual emancipation.

Johan August Arfwedson, the discoverer of lithium, was born at Skagerholms-Bruk, Skaraborgs Län, on January 12, 1792 (*10*). He studied chemistry under Berzelius, and it was in the latter's famous Stockholm laboratory that he made this great discovery at the age of twenty-five years. Berzelius described this chemical event in a letter to Berthollet written on February 9, 1818:

> The new alkali [said he] was discovered by Mr. Arfvedson, a very skillful young chemist who has been working in my laboratory for a

> year. He found this alkali in a rock previously discovered by Mr. d'Andrada in the mine at Utö and named by him petalite. This rock consists, in round numbers, of 80% silica, 17% alumina, and 3% of the new alkali. To extract the latter from it one uses the ordinary method of heating the pulverized rock with barium carbonate and separating from it all the earths. . .
>
> This alkali [continued Berzelius] has a greater capacity for saturating acids than the other fixed alkalies, and even surpasses magnesia. It is by this circumstance that it was discovered. For the salt with the [new] alkali as base, obtained by analysis, exceeds greatly in weight what it ought to have weighed if its base had been soda or potash. It was very natural to conclude that a salt with an alkali base which is not precipitated at all by tartaric acid ought to contain soda. So did Arfvedson at first, but, having repeated the analysis of the petalite three times with exactly the same results, he thought he ought to examine each constituent more thoroughly, and it is in consequence of such an examination that he noticed that the alkaline substance had properties different from other alkalies. We have given this alkali the name of lithion [lithia] to recall that it was discovered in the mineral kingdom, whereas the two others were [discovered] in the vegetable kingdom (*11*).



Engraved by W. T. Fry from an original picture by J. Opie, R.A.

EDWARD DANIEL CLARKE
1769–1822

English mineralogist and traveler. One of the founders of the Cambridge Philosophical Society. One of the first chemists to analyze the lithium mineral petalite. His "Travels in Various Countries of Europe, Asia, and Africa" contains intimate glimpses of many contemporary scientists and their laboratories. *See* ref. (*49*).

Arfwedson's own account of his analysis of petalite is to be found in the *Annales de Chimie et de Physique* for 1819. He found that it contained silica, alumina, and an alkali metal which he tried to determine by weighing it as the sulfate.

> But [said he] it was still necessary to learn the base of the salt. Its solution could not be precipitated either by tartaric acid in excess or by platinum chloride. Consequently it could not be potassium. I mixed another portion of a solution of the same salt with a few drops of pure potash, but without its becoming cloudy. Therefore it contained no more magnesia: hence it must be a salt with soda for a base. I calculated the quantity of soda which would be necessary to form it; but it always resulted in an excess of about 5 parts in 100 of the

> mineral analyzed. Therefore, since it seemed probable to me that the different substances might not have been well washed, or that the analysis might not have been made with sufficient precision in other respects, I repeated it twice more with all the care possible, but always with results very little different. I obtained: Silica: 78.45, 79.85; Alumina: 17.20, 17.30; Sulfate: 19.50, 17.75. At last, having studied this sulfate more closely, I soon found that it contained a definite fixed alkali, whose nature had not previously been known (*21*).

Petalite is now known to be lithium aluminum silicate, $LiAl(Si_2O_5)_2$.

On April 22, 1818, Berzelius wrote to his London friend, Dr. Marcet. that Arfwedson had also found lithium in spodumene and lepidolite, and that the former contains about 8 per cent of this metal, whereas the latter contains about 4 per cent. In the spring of the memorable year (1824) that Wöhler spent at Stockholm, he accompanied a distinguished group of Swedish chemists, including Berzelius, Hisinger, Arfwedson, and C. Retzius, on a holiday excursion to Utö Island, about two miles out from shore in the Baltic Sea. The island interested them greatly, not only because of its rich iron mines, but also because of its rare minerals, including petalite and spodumene, in which Arfwedson had found the new alkali metal (*9*). Lepidolite is also found on this island (*12*).

Arfwedson also studied the most important lithium salts, and his results were quickly confirmed by Vauquelin (*13*). Lithium differs from potassium in that it does not give a precipitate with tartaric acid, and from sodium in that its carbonate is only sparingly soluble. The beautiful red color which lithium salts impart to a flame was first observed in 1818 by C. G. Gmelin (*14*), (*25*).

Arfwedson and Gmelin tried in vain to isolate lithium metal. After failing to reduce the oxide by heating it with iron or carbon, they tried to electrolyze its salts, but their voltaic pile was not sufficiently powerful (*14*). W. T. Brande succeeded in decomposing lithia with a powerful battery and obtained a white, combustible metal, and Davy also obtained a small amount of lithium in the same manner (*14*), (*15*), (*31*), (*32*), (*33*).

Although these early investigators obtained only an extremely small quantity of the metal, Bunsen and Matthiessen succeeded in 1855 in preparing enough of it for a thorough study of its properties (*16*). They accomplished the reduction by heating pure lithium chloride in a small thick-walled porcelain crucible with a spirit lamp such as Berzelius used, while a current from four to six carbon-zinc elements (Bunsen cells) was passed through the molten mass. After a few seconds they saw a fused, silver-white regulus form at the cathode and build up in two or three minutes to the size of a pea. They carefully removed the globule with an iron spoon, placed it under petroleum, and repeated the operation every three minutes until they had reduced an ounce of lithium chloride (*16*). They also showed that lithium, although it was first found in the mineral kingdom, is widely distributed in all three of the natural realms.

That the famous mineralogist, the Abbé Haüy, held Arfwedson in high esteem is evident from his letter of June 13, 1820, in which he said to Berzelius, "Be so kind, Monsieur, as to offer to M. Arfvedson, of whom it suffices to say that he is your worthy pupil, the assurance of the profound esteem and distinguished respect which I bear him" (*17*).

In the same year Arfwedson bought an iron-works (*forge de feu*) and a large estate at Hedensö in the province of Södermanland, which caused Berzelius to fear lest this promising young chemist might abandon his scientific career (*17*). Perhaps his misgivings were well founded, for Thomas Thomson, after mentioning Arfwedson's experiments on the oxides of uranium* and on the action of hydrogen on metallic sulfates, said, "He has likewise analyzed a considerable number of minerals with great care; but of late years he seems to have lost his activity. His analysis of chrysoberyl does not possess the accuracy of the rest; by some inadvertence, he has taken a compound of glucina and alumina for silica" (*18*). Arfwedson died at his Hedensö estate on October 28, 1841 (*10*).

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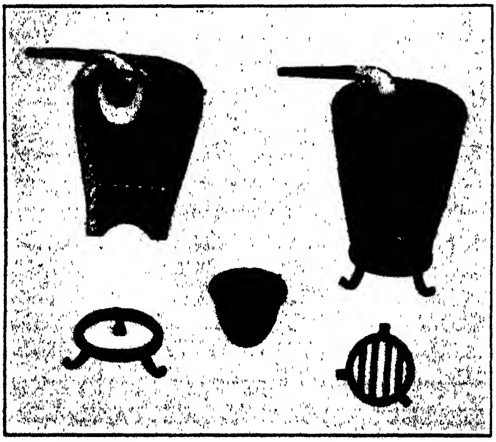

XVI. J. A. ARFWEDSON AND HIS SERVICES TO CHEMISTRY*

Although the histories of chemistry devote but little space to the work of J. A. Arfwedson, the discoverer of lithium, Berzelius' correspondence, travel-diary, and autobiography contain much interesting information about him. The superb biography of Berzelius which the late H. G. Söderbaum completed near the close of his life also throws much light on Arfwedson's chemical activity.

. . . . . .

Johan August Arfwedson was born in January, 1792,† (*1*), (*2*), on the family estate at Skagerholms-Bruk in Skaraborg County, Sweden. Until the age of fourteen, he was educated at home, and in 1806 he entered the college (högskolan) at Upsala. After completing the mining course at Upsala and the mining examinations, he entered the Royal Bureau of Mines at Stockholm, where he served as secretary at the Bureau, and still found time to carry on research in chemical analysis in Berzelius' famous laboratory. When the twenty-five-year-old Arfwedson entered this laboratory early in 1817, he had among his classmates Count H. G. Trolle-Wachtmeister, ten years his senior, and Lieutenant C. A. Arrhenius, the discoverer of gadolinite, who was then sixty years of age.

Arfwedson immediately set to work analyzing meïonite and leucite (*3*), (*4*), (*5*). He observed that although the leucite was very infusible, the meïonite melted readily before the blowpipe, swelled, and formed an enamel. Since his analysis of meionite agreed closely with Klaproth's analysis of leucite, Arfwedson analyzed a specimen of leucite and found these two minerals to be very similar in composition, except that the leucite contained no lime. Suspecting, therefore, that the lime must be the cause of the meïonite's fusibility, he mixed a little lime with the leucite, after which it, too, could be easily melted.

In the autumn of the same year, Arfwedson completed a beautiful research on the oxides of manganese. He determined the per cent of manganese in the brown powder obtained by igniting manganous oxide and in the black powder, manganic oxide, obtained by evaporating this brown manganosic oxide with nitric acid and gently igniting the residue. Since he found it difficult to get the black powder of constant composition, he recommended that in analytical work the oxide should always be strongly ignited and weighed as manganosic [mangano-manganic] oxide, Mn_3O_4.

Arfwedson also observed that the ratio of the oxygen in manganous oxide to the oxygen in manganic oxide is as 1 to $1^1/_2$, a relation which the modern chemist expresses in the formulas MnO and Mn_2O_3. He realized

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* Presented by Mary E. Larson and the author before the Divisions of History of Chemistry and Chemical Education at the Midwest Regional Meeting of the A. C. S., Omaha, Nebraska, April 30, 1937.

† Söderbaum (*1*) and Leijonhufvud (*2*) give the date of Arfwedson's birth as January 4th; the unsigned obituary (*4*) in the *Kongl. Vet. Acad. Handl.* gives it as January 12th.

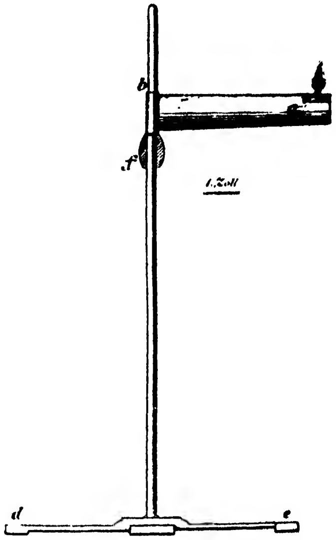
that manganosic oxide must be a compound of these two oxides, and reasoned that "if this compound, like ferrous-ferric oxide, may be supposed to be of such composition that the oxide contains twice as much metal and three times as much oxygen as the protoxide, this compound consists of 72.82 per cent metal and 27.18 per cent oxygen . . . I have called this oxide *oxidum manganoso-manganicum* because of its resemblance to ferroso-ferric oxide, the composition of which Herr Professor Berzelius described in his *Attempt to lay the foundations of a purely scientific system for Mineralogy*, page 92."

Courtesy Mr. Carl Björkbom, Royal Library, Stockholm

JOHAN AUGUST ARFWEDSON, 1792–1841

This lithograph by Fehr and Müller of Stockholm was labeled by Berzelius "Reskamraten Arfvedson" (traveling companion Arfvedson). Berzelius placed it in the manuscript of his travel diary "Reseanteckningar."

Manganosic oxide is now known to contain only 72.03 per cent of manganese. Since Arfwedson obtained 1.0735 grams of manganosic oxide by igniting one gram of manganous oxide, which is in good agreement with the value now accepted (1.0752 grams), his experimental work must have been excellent. In computing the per cent of manganese in manganosic oxide, however, he made the mistake of accepting 21.88 per cent as the oxygen content of manganous oxide, a value which Professor Johann Friedrich John of Berlin had obtained by the analysis of manganous sulfate. Arfwedson determined the composition of manganous oxide by passing hydrogen chloride over a weighed portion of manganous carbonate, treating the resulting manganous chloride with an excess of silver nitrate, and weighing the silver chloride. Although his value of 22.14 per cent oxygen in manganous oxide was somewhat better than that of John (the value now accepted is 22.56 per cent), Arfwedson lacked confidence in it and stated, "I have reason to suspect a slight admixture of oxide in the muriate I investigated, and therefore the result of my analysis is probably less reliable." In September, 1817, Berzelius reported Arfwedson's research in letters to Dr. Marcet and Gay-Lussac (*6*), and in the following year Arfwedson published it in the *Afhandlingar i Fysik, Kemi och Mineralogi* (*7*), the editorial staff of which he had recently joined.



From Berzelius' "Lehrbuch der Chemie"

BERZELIUS' BLOWPIPE LAMP

When he had completed the manganese research, Berzelius set him to work at analyzing a new mineral, petalite, from the iron mine on Utö, one of the many rocky islands or skerries which comprise Stockholm's superb archipelago. Arfwedson fused the petalite with potassium carbonate, determined the silica in the usual manner, and precipitated the alumina with ammonium carbonate. His analysis totaled only 96 per cent. Surprised to find such a large loss in such a simple analysis, he decomposed the petalite with barium carbonate. After removing the silica and alumina and the barium sulfate obtained by adding excess sulfuric acid, he evaporated the washings, volatilized the ammonium salts, and found a fused residue of a soluble, nonvolatile sulfate. Since an aqueous solution of this salt gave no precipitate with tartaric acid, "platina solution," or caustic potash, the base could be neither potash nor magnesia. Arfwedson therefore assumed that the salt must be sodium sulfate, but when he calculated his results on that assumption, his analysis totaled about 105 per cent. Thinking that this excess weight must be due to improper washing of his precipitates, he repeated the analysis twice and obtained in duplicate determinations 19.500 and 17.75 per cent of the unknown sulfate.

In a letter to Wilhelm Hisinger, who was then analyzing the same mineral, Berzelius wrote on January 12, 1818, ". . . All these facts have led us to believe that petalite perhaps contains a new alkali . . . of such great saturating capacity that, when the salt is computed as a sodium salt, the excess in weight arises through the fact that the salt contains much less base than a sodium salt. If this be true, Arfwedson has had the good fortune to make in his second mineralogical analysis one of the most remarkable discoveries which can be made in this manner . . ." (*3*). Berzelius also announced Arfwedson's discovery of lithium to Dr. Marcet and Count Berthollet in the same letters in which he mentioned his own discovery of selenium (*8*). Arfwedson's announcement of the discovery was published in the *Afhandlingar* in the same year (*9*). According to Dr. Söderbaum (*3*), Berzelius himself deserves a great deal of credit for the discovery of lithium as well as selenium, but was generous enough to let the lithium research be published under Arfwedson's name alone.

Arfwedson prepared lithium acetate, ignited it, and noted the insolubility of the resulting lithium carbonate in water and its action on platinum. He also prepared and studied the bicarbonate, sulfate, nitrate, chloride, tartrate, borate, hydroxide, and a double sulfate which he reported as lithium alum. He mentioned that lithium hydroxide is much less soluble than the other caustic alkalies and that it has a greater "saturation capacity" [lower equivalent weight] than they. Because of its ability to form deliquescent salts with nitric and hydrochloric acids, Arfwedson recognized the close relation between the new alkali and the alkaline earths, especially magnesia.

His attempt to decompose the new base with Berzelius' galvanic battery of fifty pairs of plates in an electrolyte of sodium chloride was unsuccessful. As early as 1818, however, Sir Humphry Davy obtained a minute amount of lithium metal (*10*). When he passed a current through fused lithium carbonate in a platinum capsule, "the alkali decomposed with bright scintillations, and the reduced metal being separated, afterward burnt. The small particles which remained a few moments before they were reconverted into alkali . . . were . . . very similar to sodium. A globule of quicksilver made negative and brought into contact with the alkaline salt, soon became an amalgam of lithium, and had gained the power of acting on water. . ."

Most standard works of reference also contain incomplete statements that lithium was isolated by Brande (or Brandes) and refer to Scher., **8,** 120 or Schweigger's J., **8,** 120. The correct reference is Scherer's *Allgemeine Nordische Annalen der Chem.*, **8,** 120 (1822), which merely states that W. T. Brande used a voltaic pile to prepare lithium as a shining, white, combustible metal and refers to the second London edition of his "Manual of Chemistry," Volume 2, page 57. This edition was published by John Murray in 1821. Brande's complete statement therein is as follows: "When lithia is submitted to the action of the Voltaic pile, it is decomposed with the same phenomena as potassa and soda; a brilliant white and highly combustible metallic substance is separated, which may be called *lithium*, the term *lithia* being applied to its oxide. The properties of this metal have not hitherto been investigated, in consequence of the difficulty of procuring any quantity of its oxide."*

In 1821 Arfwedson published a supplementary note to his lithium research (*11*), in which he stated that the salt which he had previously reported as lithium acid sulfate must be the normal sulfate and that the double sulfate he had at first taken for lithium alum was really potassium alum resulting from a trace of potassium in his alumina.

In the summer of 1818 Arfwedson went to England, taking with him specimens of Berzelius' new element selenium to present to Dr. Marcet, Sir Humphry Davy, and Dr. W. H. Wollaston as gifts from the discoverer. Berzelius met him there later and accompanied him on visits to Dr. Wollaston, William Prout, Sir Joseph Banks, F. C. Accum, William Allen, and the geologist John Farey, Senior. In company with Berzelius he studied at first hand the soda-water, gas, and brewing industries of England. In October of the same year the aged Abbé R.-J. Haüy of Paris entertained Berzelius and Arfwedson and gave them some inspiring lessons on mineralogy (*12*).

In June, 1819, Berzelius, Arfwedson, Alexandre and Adolphe Brongniart, and several other scientists made a geological tour of the Fontainebleau Forest and the country surrounding Clermont. Part of the journey was made in a crowded diligence in which "Arfwedson's slender form became still more compressed." At the inn in Clermont, Arfwedson, Almroth, and Berzelius finally relinquished one of their two wax candles to the insistent maid servant, who needed it for another guest, and continued their studies by the light of Berzelius' famous blowpipe lamp.

The Mont-Dore region could be explored only on horseback. "I cannot mention," said Berzelius, "all the troubles I had (*1*) in getting my left foot up into its stirrup and (*2*) in throwing the right one so high up into the air that it arrived right over the little portmanteau which was tied back of the saddle . . . However, after several attempts, and after Almroth and Arfwedson had laughed to their hearts' content at my awkwardness, I finally succeeded."

On their journey to le Puy, their fellow passengers were good-natured, inquisitive peasants who thought the Swedish language was a kind of French patois. "Arfwedson," said Berzelius, "was, in their opinion, a prince, for he was wearing in the cabriolet the same suit he wore on the streets of Paris, whereas Almroth and I had adapted ourselves more to the dirty, careless traveling costume of the French."

In Lyons, Arfwedson and Berzelius observed the manufacture of silk and velvet in the homes of the workers. In Geneva they visited Dr. and Mrs. Alexandre Marcet. While they were in Zurich, Professor M. A. Pictet of

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* This may serve as a correction to "The Discovery of the Elements," 3rd ed., p. 125.

Geneva announced to them that they had both been elected to honorary membership in the Helvetian Scientific Society.

To simplify their journey across Prussia and homeward through Sweden, Arfwedson bought a fine carriage in Dresden. Berzelius and he visited the porcelain works at Berlin, where Berzelius bought several porcelain stopcocks and was delighted to find them completely air-tight.

After their return to Stockholm in the winter of 1819, Arfwedson set up his own laboratory and equipped it with apparatus he had bought during his travels. In the following year he purchased a handsome estate at Hedensö (Heden's Island), where he equipped another chemical laboratory. However, since he owned the Näshulta Works and mill in Södermanland near Hedensö and shares in the Gravendal Works in Kopparberg and industrial plants at Skagerholm and Brunnsberg, his executive duties left him little time for research.

On April 18, 1821, he was elected to membership in the Swedish Academy of Sciences. In the same year he published some analyses of cyanite from St. Gotthard and Rörås and nepheline and sodalite from Vesuvius (*13*). In 1822 he published analyses of cinnamon stone, chrysoberyl, and boracite (*14*). He found the cinnamon stone which Berzelius had brought back from Vermland to be a calcium aluminum iron silicate and regarded it as a true garnet like the one from Ceylon which Klaproth had analyzed.

Arfwedson's analysis of Brazilian chrysoberyl was severely criticized by Thomas Thomson, who said that "by some inadvertence, he has taken a compound of glucina and alumina for silica" (*15*). Glucina, or beryllia, had been discovered by N.-L. Vauquelin nearly a quarter of a century before (*16*).

Arfwedson fused the chrysoberyl three times with caustic potash in a silver crucible. Since a portion of the melt corresponding to about 18 per cent of the mineral failed to dissolve in hydrochloric acid, he reported this residue as silica. It is now known that beryllium hydroxide, when freshly precipitated, dissolves readily in hydrochloric acid, but becomes after a time almost completely insoluble in it (*17*). Therefore, it is probable that Arfwedson's "silica" was really the beryllium hydroxide. He then precipitated the alumina by adding ammonium hydroxide to the acid filtrate. To satisfy himself of the purity of his alumina, he saturated the alkaline solution with hydrochloric acid until the precipitate dissolved, and added a large excess of ammonium carbonate. "Had any glucina [beryllia] or yttria existed in the matter," said Arfwedson, "it would have been dissolved by this excess of carbonate of ammonia, and would have fallen when the filtered liquid was boiled till the excess of ammonia was driven off; but the liquid stood this test without any precipitate appearing." Arfwedson was evidently unable to detect beryllia here because he had already filtered it off and reported it as silica. When the American chemist Henry

Seybert analyzed the same mineral in 1824 he found it to contain from 15 to 16 per cent of beryllia (*22*).

In 1822 Arfwedson published his paper on uranium (*18*). More than thirty years before, Klaproth had heated a paste made with uranic oxide and linseed oil, and obtained a brown powder with a metallic luster, which he regarded as metallic uranium. Although others had used carbon crucibles in their attempts to reduce uranium oxide to the metal, Arfwedson used hydrogen. He placed a weighed portion of ignited "uranous oxide" [uranosic, or uranous-uranic oxide] in a bulb blown out at the center of a piece of barometer tubing, drove off the moisture, and passed dry hydrogen over it. As soon as the air had been removed, he heated the bulb with an Argand spirit lamp. A vigorous reaction took place, and in a few minutes the green "uranous oxide" had been changed to "a powder of a liver-brown color," which Arfwedson believed to be uranium metal.

He also prepared the "potash muriate of uranium" [potassium uranyl chloride, $K_2(UO_2)Cl_4$], and attempted to analyze it by reduction with hydrogen just as Berzelius had analyzed potassium chlorplatinate (*19*). As Arfwedson passed hydrogen over the strongly heated salt, it continued to lose hydrochloric acid for more than two hours. After cooling the apparatus, he washed out the potassium chloride and the undecomposed salt and obtained a dark, crystalline powder with a metallic luster. When this was heated, it became converted into green "uranous oxide" [uranosic oxide]. During this change, 100 parts of the so-called "metal" [uranous oxide] gained 3.7 parts of oxygen. This was evidently the reaction: $3UO_2 + O_2 = U_3O_8$, in which 100 parts of uranous oxide actually gain 3.95 parts of oxygen; 100 parts of true uranium metal would have gained 17.9 parts of oxygen. Arfwedson, however, did not believe that his powder could be an oxide, for, according to Sir Humphry Davy's new theory regarding the composition of muriatic [hydrochloric] acid, the double chloride of uranium and potassium contained no oxygen.

Although Arfwedson, Klaproth, Berzelius, and many other eminent chemists long regarded this crystalline powder as the metal, E. M. Peligot in 1841 obtained the true metal. When he heated uranous oxide with carbon in a current of chlorine, he obtained carbon monoxide, carbon dioxide, and a green crystalline compound which is now known to be uranous chloride, UCl_4. Since the evolution of carbon dioxide and carbon monoxide showed that the so-called "uranium" must contain oxygen, Peligot heated the uranous chloride with potassium and succeeded for the first time in preparing and studying true metallic uranium. As early as 1824, however, Friedrich Stromeyer had doubted that Arfwedson's "uranium" was the metal (*23*).

When Arfwedson tried to analyze lead uranate by reducing it with hydrogen, it gained weight and became hot. When he placed the reduced mass on paper, he was astonished to see it burst into flame. He also prepared other pyrophoric alloys of uranium in the same way. "The uranium alloys," said he, "absorb oxygen again at ordinary temperatures, become ignited, and thus constitute a peculiar kind of pyrophors which are not inferior in flammability to those already known."

In 1822 Arfwedson published a paper on the decomposition of sulfates with dry hydrogen (*20*). In the following year the British mineralogist H. J. Brooke (1771–1857) described a new mineral, *arfwedsonite* (*21*). "The benefits which mineralogy has derived from the labours of Mr. Arfwedson," said he, "have induced me to associate his name with this mineral, which is from Greenland, and is black and foliated, and has been hitherto called ferriferous hornblende . . ."

In the autumn of 1824 Arfwedson helped Berzelius and Wilhelm Hisinger arrange the mineral collection of the Academy of Sciences according to Berzelius' chemical system. Two years later Berzelius visited Arfwedson at Hedensö. "This," said he, "is a most beautiful place, and Arfwedson and his wife have improved it since I was here last time. Inside there reigns extreme neatness and a degree of luxury which could be much less and still be sufficient" (*3*).* Berzelius' pleasure was marred, however, by an attack of gout which did not yield even when Arfwedson himself applied nine leeches to the affected knee.

Although Arfwedson's business interests more and more distracted his attention from chemical research, this was not caused by the love of money. When one of his uncles bequeathed him the magnificent Forssby estate with its precious collection of oil paintings, Arfwedson allowed this inheritance to be shared according to law with the other heirs.

In the last year of his life, the Swedish Academy of Sciences awarded him its large gold medal (*2*) in honor of his discovery of lithium. He died at Hedensö on October 28, 1841, and was survived by his wife and three sons. The *Vetenskapsacademiens Handlingar* for that year contained the following tribute to his memory: "His love of order gave an impress of neatness not only to his person but also to everything about him. He had a pleasant manner; when different points of view were exchanged, he expressed himself with a deliberateness which was not compliance and with a thoroughness which showed deep thought. One may venture to say that, because he was obliged to devote his time to the management of a considerable fortune, . . . the science to which he devoted himself in his youth lost much (*4*)."

In conclusion we wish to thank Mr. Carl Björkbom of the Royal Library at Stockholm and Miss Amy Wästfelt of Upsala for their kind assistance.

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* Letter of Berzelius to Carl Palmstedt, July 26, 1826.

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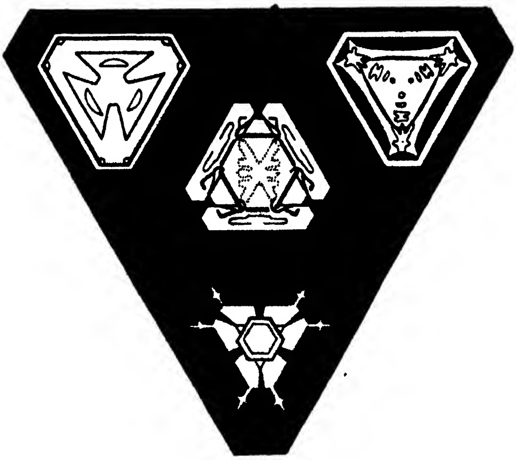


XVII. THE ALKALINE EARTH METALS AND MAGNESIUM AND CADMIUM

The isolation of the alkaline earth metals required the combined genius of Davy and Berzelius. After the latter had succeeded in decomposing lime and baryta by electrolyzing a mixture of the alkaline earth and mercury, Davy was able in 1808 to prepare the amalgams in larger quantity and, by distilling off the mercury, to isolate the metals, strontium, barium, calcium, and magnesium. In the year 1817 a number of preparations of zinc oxide sold by German apothecaries were confiscated by the inspectors, who found that zinc carbonate had been substituted for the oxide, that the carbonate became yellow upon heating, and that, when hydrogen sulfide was passed into an acid solution of the carbonate, a yellow precipitate resembling arsenious sulfide was thrown down. The researches of Dr. Stromeyer, Dr. Roloff, and Mr. Hermann proved, however, that this yellow precipitate was not arsenic sulfide, but the sulfide of an unknown metal. Thus the good name of the manufacturing pharmacies was restored, and the chemical world was enriched by the discovery of the new element, cadmium.

. . . . . .

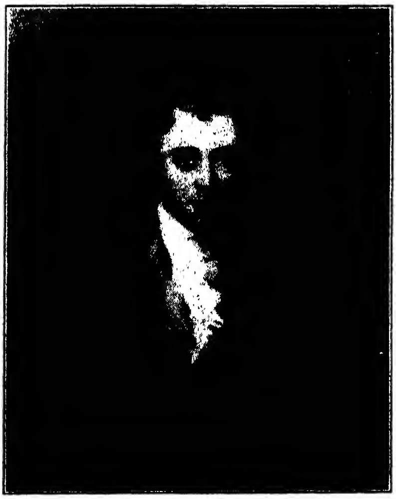
If matter cannot be destroy'd,
The living mind can never die;
If e'en creative when alloy'd,
How sure its immortality!

Then think that intellectual light,
Thou loved'st on earth is burning still,
Its lustre purer and more bright,
Obscured no more by mortal will (*1*).

Calcium

Although the ancients had many uses for lime, they knew nothing of its chemical nature. The *De Re Rustica* of Marcus Porcius Cato the Censor (234–149 B.C.), the *De Architectura* of Marcus Vitruvius Pollio (who lived in the reign of Augustus), and the *Historia Naturalis* of Pliny the Elder all discuss the preparation, properties, and uses of lime (*44*), (*45*), (*46*) Vitruvius noticed that lime from the kiln, although it was as bulky as the original limestone, had "lost about one third of its weight owing (he said) to the boiling out of the water" (*47*).

George Ernst Stahl (1660–1734) thought that in the slaking of this substance the earthy element combined with the watery element to form a salt. He admitted that there are distinct earths that might be converted into metals by combining with phlogiston. Although most eighteenth-century chemists thought that lime and baryta were elements, Lavoisier believed them to be oxides (*2*), (*12*). "It is probable," said he, "that we know only part of the metallic substances which exist in Nature; all those, for example, that have more affinity for oxygen than for carbon are not capable of being reduced or brought to the metallic state, and they must not present themselves to our eyes except in the form of oxides, which we do not distinguish from the earths. It is very probable that baryta, which we have just classified with the earths, is one of these; it presents experimentally properties which closely ally it with metallic substances. It is possible, strictly speaking, that all the substances which we call earths may be simply metallic oxides irreducible by the methods we employ" (*12*). Caspar Neumann made some elaborate but unsuccessful attempts to obtain a metal from quicklime (*3*), but for this difficult reduction new methods, new apparatus, and the genius of a Davy were required.



From Muspratt's "Chemistry, Theoretical, Practical and Analytical"

SIR HUMPHRY DAVY
1778–1829

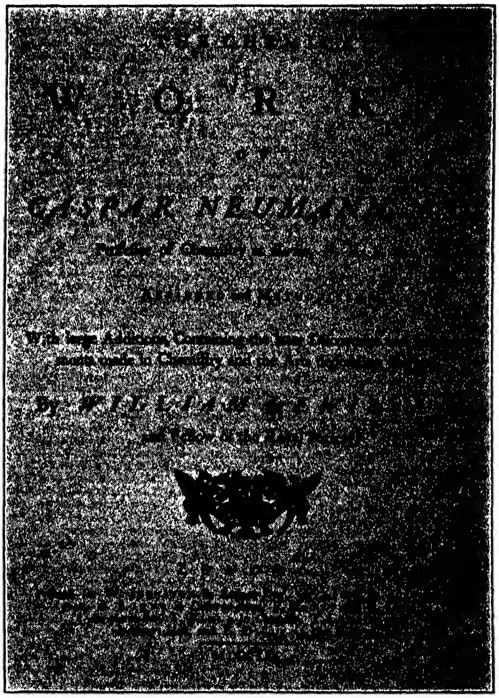
Professor of chemistry and lecturer at the Royal Institution, London. Scientist, poet, and humanitarian. Donor of the Davy Medal.

Sir Humphry's ardent nature could not rest content with his recent triumphs over sodium and potassium. With a conqueror's enthusiasm he pushed ahead toward the still more difficult task of decomposing the alkaline earths. In his first attempts he passed a current through the moist alkaline earth, which was protected from the air by a layer of naphtha. There was slight decomposition, but any metal that may have been formed combined immediately with the iron cathode (*3*).

Davy then tried to use potassium directly as a reducing agent. "I heated potassium," said he, "in contact with dry, pure lime, barytes, strontites, and magnesia, in tubes of plate glass; but as I was obliged to use very small quantities, and as I could not raise the heat to ignition without fusing the glass, I obtained in this way no good results." Although the potassium attacked the earth and the glass, no distinct metallic globules were obtained (*3*).

The method he finally adopted was to mix the non-conducting, dry earth (lime, strontia, or baryta) with excess potash and fuse it. When he covered the alkaline mixture with naphtha and passed an electric current through it, he soon saw metallic globules rising and bursting into flame, but when the flame died out, there remained nothing except potash and the alkaline earth with which he had started (*2*), (*3*).

Although greatly disappointed over this failure, Sir Humphry soon thought out another plan of attack. This time he mixed lime with mercuric oxide and obtained a small amount of calcium amalgam. He also made similar alloys of the other alkaline earths with mercury, silver, tin, and lead, but never obtained enough of the alloy to permit the isolation of the alkaline earth metal. In May, 1808, however, Berzelius wrote Davy that he and Dr. Pontin, the king's physician, had decomposed lime by mixing it with mercury and electrolyzing the mixture, and that they had been equally successful in decomposing baryta and preparing barium amalgam (*2*), (*13*).



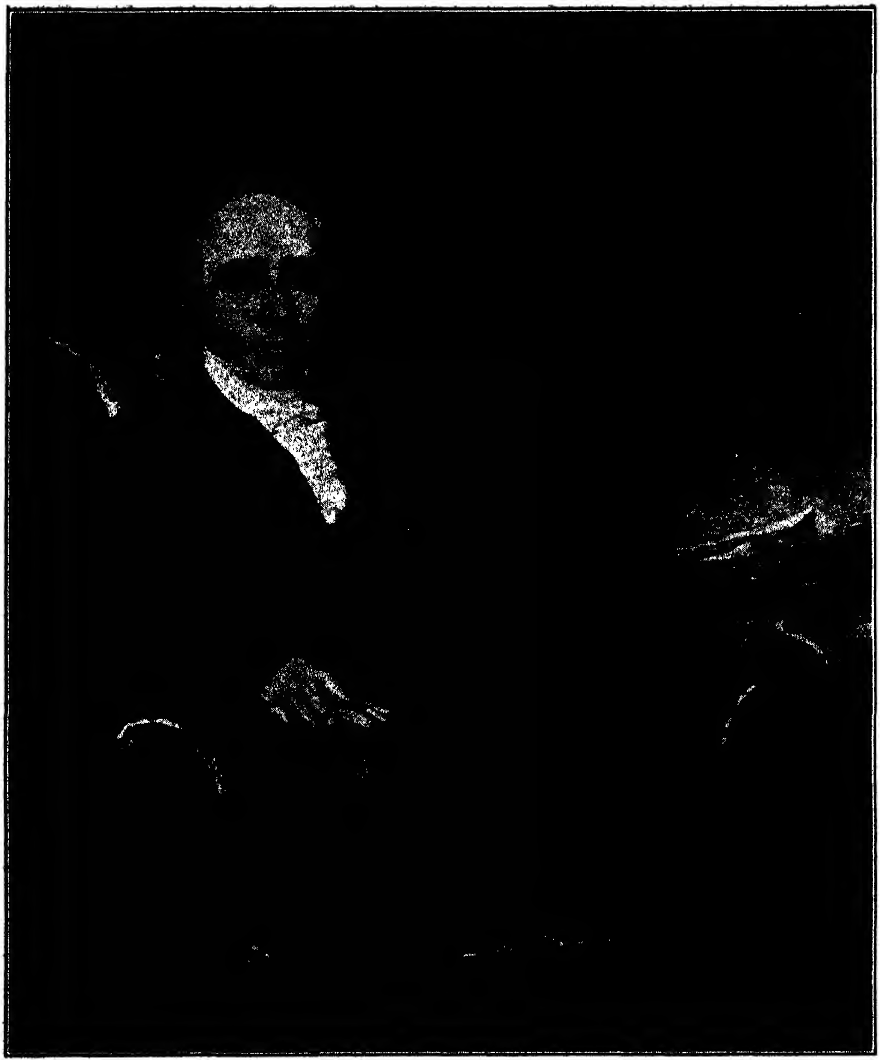
Title Page of the "Chemical Works of Caspar Neumann" (1683–1737)

Apothecary and professor of chemistry at Berlin. His writings were carefully studied by Scheele and Davy.

With the help of this suggestion, Davy finally worked out a method of obtaining the alkaline earth metals themselves. He mixed the moist earth with one-third its weight of mercuric oxide, and placed it on a platinum plate connected to the positive pole of a powerful battery. He then hollowed out a little cavity in the center of the mixture, and poured a globule of mercury into it in order to make possible the use of a heavy current from "a battery of five hundred." A platinum wire dipping into the mercury was connected to the negative pole. By this means Sir Humphry obtained enough of the calcium amalgam so that he could distil off the mercury and see for the first time the silvery-white metal, calcium (*2*), (*3*), (*7*).

In his letter of July 10, 1808, Davy acknowledged his indebtedness to Berzelius and Dr. Pontin. After describing his early failures he said:

> Since I have been favoured with your papers, I have, however, made new and more successful attempts, and by combining your ingenious



Courtesy Sir James C. Irvine

THOMAS CHARLES HOPE
1766-1844

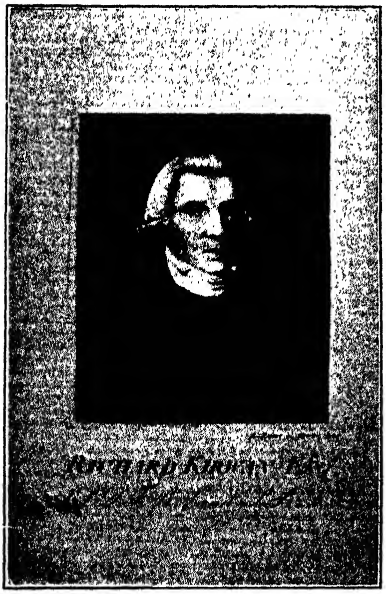
Scottish chemist and physician. Successor to Dr. Joseph Black at Edinburgh. The first chemist in Great Britain to teach Lavoisier's views on combustion. Hope and Dr. Adair Crawford were the first to distinguish between baryta and strontia.

mode of operating with those that I before employed, I have succeeded in obtaining sufficient quantities of amalgams for distillation. At the red heat the quicksilver rises from the amalgams and the bases remain free. The metals of strontites, barytes, and magnesia are all that I have experimented upon in this way; but I doubt not the other earths will afford similar results. . . . I consider this letter as addressed in common to you and your worthy fellow labourer, Dr. Pontin, to whom I must beg you to present my compliments" (*14*).

DR. PONTIN (M.M. AF PONTIN)
1781–1858

Physician to the King of Sweden. He collaborated with Berzelius in preparing amalgams of calcium and barium by electrolyzing lime or baryta in presence of mercury. Author of a biography of Berzelius.

Pure calcium cannot be prepared by the method of Davy and Berzelius, and a successful commercial process was not perfected until nearly a century later (*32*).



RICHARD KIRWAN
1733–1812

Irish chemist. Author of a treatise on water analysis, which is one of the first books on quantitative analysis. Famous for his early researches on strontia.

Barium

Early in the seventeenth century Vincenzo Casciarolo, a shoemaker and alchemist in Bologna, noticed that when heavy spar is mixed with a combustible substance and heated to redness, the resulting mixture, which became known as the "Bologna stone," emits a phosphorescent glow. W. Derham in 1726 gave the following account of the "Bolognian phosphorus": "This stone is found in three Places near the City of Bologna; the first is called Pradalbino; the second is a small Brook near the Village Roncaria; the third is called Monte Paterno, and is most noted for these Stones; . . . It's known by a Glittering. . .which surprizes the eye. It was first found out by . . . Vincenzo Casciarolo, a Cobler, but ingenious, and a Lover of Chymistry; who, trying several Experiments with these Stones, by Chance happened on this Way of preparing them, so as to make them shine in the Dark, after they had been some Time exposed to the Sun. . . It's usually no bigger than an Orange; and tho' Licetus affirms, there never was any greater than that in Androvandus' [Ulisse Aldrovandi's] Museum, weighing about two Pound and a half; yet the Author hath had of five Pound. It's very heavy, considering the Bulk, as being probably compounded of several mineral Substances. . . When It's well prepared, it leaves a Lustre in the Superficies, and is enlightened, not only by the Sun, but the Moon, and a Fire; but by these not so strongly, as the Sun. The Light, tho' it appear like a Coal, yet is not sufficient to read with, unless applied close to the Word. It will not retain the Light very long, at one Time, nor its Vertue above five or six Years. . ." (*37*). Derham also described in great detail the method of preparing the "Bolognian phosphorus" from the mineral.

Naturalist's Library, vol. 7

ULISSE ALDROVANDI
(*or* ALDROVANDUS)
1522–1605 (?)

Italian scholar and collector, well versed in all branches of natural science. Professor of pharmacognosy at Bologna. Founder of a great botanical garden, museum, and library, which he bequeathed to the state. Volume 4 of the superbly illustrated 1642 folio edition of his complete works contains an account of the "Bologna stone," barite (*De lapide illvminabili*).

A seventeenth-century item in the *Philosophical Transactions* states that "Though several Persons have pretended to know the Art of Preparing and Calcining the Bononian Stone, for keeping a while the Light once Imbibed, yet there hath been indeed but One who had the true Secret of performing it. This was an Ecclesiastick, who is now dead, without having left that Skill of his to any one. . .S. [Marcello] Malpighi takes notice, That one S. Zagonius had a way of making out of the Bononian Stone Calcin'd, Statues and Pictures variously Shining in the Dark. But he adds (to our sorrow) that that Person lately Dy'd, without discovering to any Body his Method of Preparing it" (*58*). In his "History . . . of vision, light, and colours," Joseph Priestley stated that "the best method of preparing the Bolognian stone had been kept a secret in the Zagonian family, all of whom had died without revealing it" (*59*).

Wilhelm Homberg observed that Balduin's phosphorus (anhydrous calcium nitrate) was similar to the Bolognian but shone with a somewhat feebler light. B.-B. de Fontenelle's eulogy states that Homberg "worked at

Bologna on the stone which bears the name of that city, and restored to it all its light, for the secret of it had almost been lost" (*55*). When he repeated the experiment in Paris, he was unsuccessful. Homberg himself finally found that when he ground the materials in an iron mortar, the experiment failed, but when he used a bronze mortar and pestle, he obtained a luminous product (*56*). Some impurities serve as activators for producing a high degree of fluorescence, whereas others have an inhibiting effect. Hence in the most modern plants for the manufacture of fluorescent lamps, dust must be completely excluded (*57*).

Priestley mentioned that Jacopo Bartolomeo Beccari and other scientists of Bologna in 1711 "took a great deal of pains with the chymical analysis of this fossil, by which they thought they discovered in it some sulphur and also an *alkaline salt*" (*59*). For some time this mineral was believed to be a kind of gypsum, but Cronstedt classified it as a special species. Marggraf showed in 1750 that it contains sulfuric acid, but he believed the base to be lime (*18*).

In his famous investigation of pyrolusite, which was published in 1774, C. W. Scheele discovered a new base, baryta, which gave a white, nearly insoluble precipitate with sulfuric acid and with vitriols (*15*), (*18*). Although he first encountered the new alkali merely as an accidental or nonessential constituent of pyrolusite, he soon received from Torbern Bergman a specimen of this mineral to which some peculiar crystals were attached. On February 28, 1774, Scheele wrote to J. G. Gahn, "Haven't you seen, Sir, on Braunstein, especially on some of it, a few white sparry crystals? You undoubtedly have. One might take it for gypsum or calcite, but incorrectly. It is the new earth itself, combined with sulfuric acid. I'm curious to know with what kind of a name Herr Professor Bergman will christen this earth. He thinks that there must be rocks which contain a great deal of this earth" (*60*). A month later, Scheele sent some of these crystals to J. G. Gahn, who found that they had the same composition as massive heavy spar, or Bologna stone.

Although baryta was at first a great rarity, Gahn's discovery of the composition of Bologna stone opened up to chemists an abundant source of it. In his letter of May 16, 1774, Scheele congratulated Gahn as follows: "I am delighted that you have discovered the presence in heavy spar of the earth I mentioned. It must therefore be named *Schwerspatherde* (earth of heavy spar). Scarcely had I investigated the crystals you sent me until I hurried to Herr Professor Bergman and received from him a piece of this spar, on which I immediately began to experiment" (*60*).

Baryta was first distinguished from lime in 1779 by Scheele, who prepared it from heavy spar, a naturally occurring barium sulfate. He reduced the sulfate to the sulfide by heating a sticky, pasty mixture of heavy spar, powdered charcoal, and honey. After decomposing the barium sulfide with hydrochloric acid, he added excess potassium carbonate to precipitate the barium as the carbonate (*15*). Metallic barium was first prepared by Sir Humphry Davy in 1808 (*2*), (*3*), (*4*).

Strontium

In about 1787 a rare mineral, which had long been exhibited in one or two collections, was brought to Edinburgh in considerable quantity by a dealer in minerals. Although some mineralogists mistook it for fluorite, most of them regarded it as a kind of "aerated barytes" (witherite, or barium carbonate). It was found in the lead mine at Strontian, Argyleshire, intermingled with the lead ore and with "calcareous and ponderous spars" (calcite and witherite) (*48*).

In 1790 Dr. Adair Crawford (1748–1795) published a paper on "The medicinal properties of the muriated barytes" (barium chloride) (*18*). "The muriated barytes exhibited in St. Thomas's Hospital since the month of May, 1789," said he, "was obtained by the decomposition of the heavy spar. Having procured some specimens of a mineral which is sold at Strontean [sic], in Scotland, under the denomination of aerated barytes, I was in hopes that the salt might be formed with less difficulty by immediately dissolving that substance in the muriatic acid. It appears, however, from the following facts, which have been verified by the experiments of my assistant, Mr. Cruikshank, as well as by my own, that this mineral really possesses different properties from the terra ponderosa [baryta] of Scheele and Bergman" (*49*).

Dr. Crawford showed in this paper that the salt (strontium chloride) obtained by dissolving the new mineral in hydrochloric acid differs in several respects from barium chloride. It is much more soluble in hot water than in cold, the strontium salt is much the more soluble in water and produces a greater cooling effect, and these two chlorides have different crystalline forms. He concluded therefore that "the mineral which is sold at Strontean [sic] for aerated terra ponderosa possesses different qualities from that earth, although at the same time it must be admitted that in many particulars they have a very near resemblance to each other." He also stated that "it is probable that the Scotch mineral is a new species of earth which has not hitherto been sufficiently examined" and that "Mr. Babington. . . has for some time entertained a suspicion that the Scotch mineral is not the true aerated terra ponderosa." In 1790 Dr. Crawford sent a specimen of the new mineral (strontianite, strontium carbonate) to Richard Kirwan for analysis (*50*).

Adair Crawford was born at Antrim, Ireland, and received his degree of doctor of medicine at Glasgow in 1780. After settling in London he became a physician at St. Thomas's Hospital, a member of the Royal College of

Physicians, and professor of chemistry at Woolwich. He died in 1795 at the estate of the Marquis of Lansdowne, near Lymington, Hants (*51*).

According to Robert Hunt, Dr. Crawford "was distinguished by his desire to be accurate in all his investigations. All his pieces of apparatus were graduated with delicate minuteness which has never been surpassed" (*52*). In his epitaph for Dr. Crawford, Mr. Gilbert Wakefield described him as follows: "In the practice of his profession intelligent, liberal, and humane; in his manner gentle, diffident, and unassuming; his unaffected deference to the wants of others, his modest estimate of himself, the infant simplicity of his demeanor, the pure emanation of kind affection, and a blameless heart rendered him universally beloved. To these virtues of the man his contemporaries alone can testify. As a votary of science and author of a treatise on Animal Heat, posterity will repeat his praise" (*51*).

Near the close of 1791, Thomas Charles Hope of Edinburgh began an elaborate investigation of the Strontian spar, the results of which he presented to the College Literary Society of Edinburgh in March, 1792, and to the Royal Society of Edinburgh on November 4, 1793. In these experiments he made a clear distinction between witherite and strontian spar (strontianite) and proved conclusively that the latter contains a new earth "strontites," or strontia (*26*), (*30*), (*48*). He noticed that strontia slakes even more avidly with water than does lime; that, like baryta, it is much more soluble in hot water than in cold; that its solubility in water is extremely great; and that all its compounds, especially the chloride, tinge the flame of a candle red. "This flame color," said Hope, "was first mentioned to me in the 1787 by an ingenious gentleman, Mr. Ash, who was then studying physic at Edinburgh." Dr. Hope also noticed the green flame color of barium and the red of calcium, which he was able to distinguish from the more brilliant red of strontium.

Although many of the properties of strontia are intermediate between those of lime and baryta, he proved that it is not a combination of the two and that it "bears repeated solutions, crystallizations, and precipitations without showing the smallest disposition to a separation of principles" (*48*). Thus it is evident that Dr. Hope foreshadowed in 1793 one of the triads which J. W. Döbereiner pointed out in 1829.

Benjamin Silliman the Elder studied at Edinburgh in 1805. "My earliest introduction," said he, "among men of science was to Dr. Thomas Hope, Professor of Chemistry &c. in the University of Edinburgh. I found him at his house in New Town and received a very kind and courteous welcome. Dr. Hope was a polished gentleman, but a little stately and formal withal. . . . He proved himself a model professor and fully entitled to act as a mentor. The professorship of chemistry was, at the time of my Edinburgh residence, very lucrative. The chair was so ably filled and the science so fully illustrated by experiments that the course drew a large audience which, at three guineas a ticket, probably gave him an income of four thousand dollars or more—some said, five thousand. He with his brother kept bachelors' hall in a handsome house on Princes Street, in the New Town. . . .

"Dr. Hope's lectures. . .were not only learned, posting up the history of the discovery, and giving the facts clearly and fully, but the experiments were prepared on a liberal scale. They were apposite and beautiful, and so neatly and skilfully performed that rarely was even a drop spilled upon the table. . . Dr. Hope lectured in full dress, without any protection for his clothes; he held a white handkerchief in his hand, and performed all his experiments upon a high table, himself standing on an elevated platform, and surrounded on all sides and behind by his pupils. . ." (*53*).

In his "Story of the University of Edinburgh," Sir Alexander Grant said that "Hope was fully alive to the importance of the quantitative age in Chemistry . . . he had learnt Lavoisier's views from himself, and in personal communication with Dalton had imbibed his ideas of atomic constitution." Professor Hope's two greatest contributions to science were his research on strontia and his observation of the curious and beneficent property that water has of attaining its maximum density at a certain temperature (now fixed accurately at 4°C.). He abandoned research, however, in order to devote all his time to the improvement of his lectures. Since he sometimes had more than five hundred students, it was necessary for him to perform the lecture experiments on a very large scale (*54*).

BENJAMIN SILLIMAN THE ELDER
1778–1864

American chemist, geologist, mineralogist, and pharmacist. This miniature by Rogers was made in 1818, the year in which Silliman founded the *American Journal of Science* (thirteen years after he had studied in Edinburgh under T. C. Hope).

Among the first to investigate strontia were F. G. Sulzer, J. F. Blumenbach, J. G. Schmeisser (*18*), Court-Apothecary J. K. F. Meyer of Stettin,

R. Kirwan (*28*), (*29*), (*50*), M. H. Klaproth (*19*), Bertrand Pelletier (*16*), J. T. Lowitz, and Fourcroy and Vauquelin (*17*).

Sir Humphry Davy isolated the metal in 1808 by the method he had used for calcium and barium (*5*), (*3*). In 1924 P. S. Danner of the University of California allowed the oxides of barium and strontium to react with magnesium or aluminum and, upon distilling, obtained both barium and strontium in a high state of purity. His method was a refinement of the one previously used by A. Guntz (*33*), (*34*).

JOHANN RUDOLPH GLAUBER
1604–1670

German chemist who detected sodium sulfate (Glauber's salt, the *enixum* of Paracelsus) in water from a spring near Vienna and introduced its use into medicine. His "Description of New Philosophical Furnaces" contains methods for the preparation of pyroligneous acid and the mineral acids.

Magnesium

During a drought in the summer of 1618 Henry Wicker (or Wickes) discovered on the common at Epsom, Surrey, a small hole filled with water. To his astonishment, not one of his thirsty cattle would drink there. This bitter water was found to have a healing effect on external sores and to be useful also as an internal medicament. By the middle of the seventeenth century, Epsom had become a fashionable spa, attracting famous visitors from the continent (*40*), (*62*).

In 1695 Dr. Nehemiah Grew published a dissertation on the medicinal value of salt from these wells (*41*). In 1726 John Toland wrote that "these aluminous waters are experienc'd to be very beneficial. . .; the salt that is chymically made of 'em being famous over all Europe" (*40*).

Since the supply of the natural salt was insufficient to meet the demand for it, it was soon superseded by an artificial product. According to Torbern Bergman, crystals of artificial Epsom salt from sea water "are sometimes so large that they are sold for Glauber's salt; and on the other hand, in France, Glauber's salt, being reduced to small speculae, by agitating it during the crystallization, is sold for Epsom salt. "These frauds," said he, "are indeed of little consequence, yet they throw a veil over the truth, and are not easily discovered"

Caspar Neumann (1683–1737) stated that the artificial Epsom salt was prepared at Portsmouth by adding sulfuric acid to the mother liquors left in the purification of sea salt imported from Spain and Portugal (*43*). He distinguished clearly between Epsom salt and the "sal mirabile of Glauber" (sodium sulfate), and stated that "The earth of the bitter purging salt is called *Magnesia alba*. . . . I have nowhere met with this earth in the mineral kingdom. . . ." He did not distinguish between magnesia alba and lime, however (*43*).

An excellent account of the early history of magnesia is to be found in Bergman's *Physical and Chemical Essays* (*42*). At the beginning of the eighteenth century, a certain canon regular sold at Rome a secret panacea called *magnesia alba*, or *Count Palma's powder*. In 1707 Michael Bernhard Valentini of Giessen revealed the method of preparing it by calcination from "the last lixivium of nitre." Two years later, Johann Adrian Slevogt of Jena gave an easier way of preparing it by precipitation. Since this powder effervesced with acids, chemists long confused it with "calcareous earth," or calcium carbonate, which they used to prepare from crabs' eyes, oyster shells, and egg shells. Friedrich Hoffman (1660–1742) observed, however, that when calcareous earth was treated with vitriolic (sulfuric) acid, it yielded an insipid salt, whereas magnesia was converted by similar treatment into an intensely bitter one (*42*).

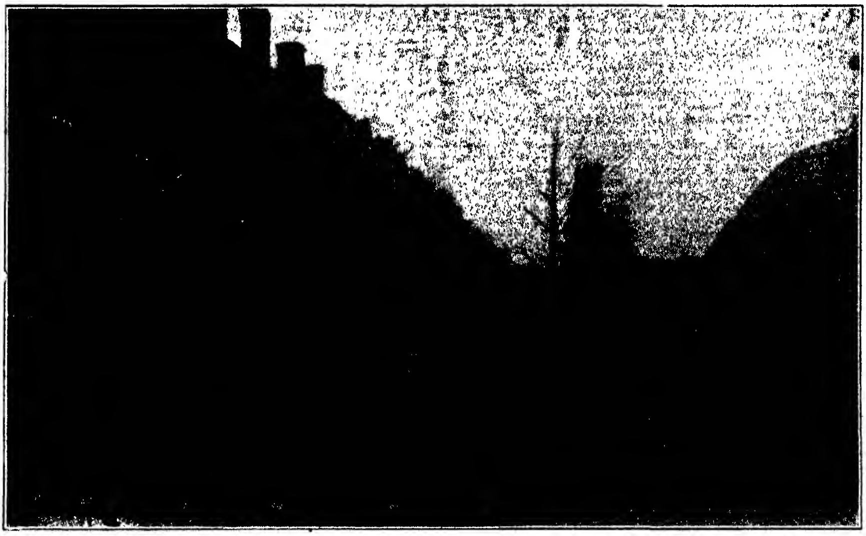
At this time it was believed that when carbonates were calcined they combined with an acrid principle from the fire to form caustic alkalies. In 1755, however, Dr. Joseph Black (*26*) of Edinburgh published a famous treatise entitled, "Experiments upon Magnesia Alba, Quicklime, and some other Alkaline Substances," in which he proved that carbonates *lose* weight during calcination and that the substance expelled is carbon dioxide, "fixed air." In this treatise he showed that magnesia is entirely different from lime, and four years later Marggraf in Berlin made the same discovery independently (*6*), (*18*), (*20*), (*21*), (*38*).

ANTOINE-ALEXANDRE BRUTUS BUSSY
1794–1882

French chemist, pharmacist, and physician. Professor of chemistry at the École de Pharmacie in Paris. He was connected with this school for more than fifty years, and for nearly thirty years he served as its director. In 1831 he obtained magnesium in coherent form.

When Sir Humphry Davy isolated a little magnesium metal in the famous experiments already described, he called it *magnium* because, as he said, the word *magnesium* is easily confused with *manganese.* Nevertheless, the name magnesium has persisted, and the metal is no longer known by the one which Davy gave it.

The quantity of metal which he prepared was very small, and it was not until 1831 that it was first prepared in a coherent form. This was done by the French chemist, Antoine-Alexandre-Brutus Bussy, who was born at Marseilles on May 29, 1794. He studied at the École Polytechnique for a time, but his interest in chemistry soon led him to abandon his military career and to become apprenticed to a pharmacist. After studying pharmacy at Lyons and at Paris he became a pupil of Robiquet, who was then a préparateur in chemistry at the École de Pharmacie. Bussy graduated in pharmacy in 1823 and received his medical degree in 1832.



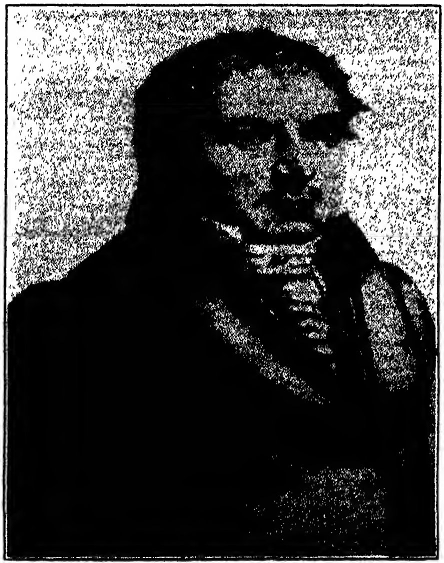
SIDE VIEW OF THE ÉCOLE SUPÉRIEURE DE PHARMACIE, SHOWING THE LABORATORIES FOR PRACTICAL PHARMACY

Although most of his researches were of a pharmaceutical nature, he published in 1831 a paper entitled "Sur le Radical métallique de la Magnésie," in which he described a new method of isolating magnesium, which consisted in heating a mixture of magnesium chloride and potassium in a glass tube. When he washed out the potassium chloride, small, shining globules of metallic magnesium remained (*8*), (*20*), (*27*).

For several years Bussy taught pharmacology in the medical school at the École de Pharmacie; and in 1856 he served as president of the Academy of Medicine. For fifty-six years he served on the editorial staff of the *Journal de Pharmacie et de Chimie*. He died at Paris on February 1, 1882, at the age of eighty-seven years (*22*).

Cadmium

Cadmium was discovered in 1817 by Dr. Friedrich Stromeyer, a professor of chemistry and pharmacy at Göttingen University. He was born on August 2, 1776, at a time when the phlogiston theory was drawing its last breath (*8*). After studying chemistry, botany, and pharmacy in his native city of Göttingen, he worked in Paris under the great master of analytical chemistry, Vauquelin. Following the example of this famous teacher, he devoted himself almost entirely to the analysis of minerals (*9*).



Science Service

FRIEDRICH STROMEYER
1776–1835

German physician, botanist, chemist, and pharmacist. Inspector-general of all the Hanoverian apothecary shops. Discoverer of the element cadmium. His collection of thirty mineral analyses is a classic of analytical chemistry.

In 1802 he became a *Privatdozent* in the faculty of medicine at Göttingen, and was rapidly promoted until in 1810 he became a full professor (*Professor ordinarius*). In the German universities, as in certain American ones, professors frequently hold government offices. Dr. Stromeyer was the inspector-general of all the apothecaries of Hanover. On an inspection trip to Hildesheim in the autumn of 1817 he noticed that a certain preparation which, according to the Hanoverian Pharmacopœia, ought to have contained zinc oxide, contained zinc carbonate instead. The events which followed were described by Dr. Stromeyer in his letter to Dr. Schweigger written on April 26, 1818:

> As I was last harvest inspecting the apothecaries' shops in the principality of Hildesheim, in consequence of the general inspection of the apothecaries of the kingdom having been entrusted to me by our most gracious Regency, I observed in several of them, instead of the proper oxide of zinc, carbonate of zinc, which had been almost entirely procured from the chemical manufactory at Salzgitter. This carbonate of zinc had a dazzling white colour; but when heated to redness, it as-

> sumed a yellow colour, inclining to orange, though no sensible portion of iron or lead could be detected in it.

In an attempt to determine why this substitution had been made, Dr. Stromeyer visited the pharmaceutical firm at Salzgitter:

> When I afterwards visited Salzgitter, during the course of this journey [said he] and went to the chemical manufactory from which the carbonate of zinc had been procured; and when I expressed my surprise that carbonate of zinc should be sold instead of oxide of zinc, Mr. Jost, who has the charge of the pharmaceutical department of the manufactory, informed me that the reason was, that their carbonate of zinc, when exposed to a red heat, always assumed a yellow colour, and was on that account supposed to contain iron, though the greatest care had been taken beforehand to free the zinc from iron, and though it was impossible to detect any iron in the oxide of zinc itself.

EXHIBIT OF DRUGS AND MEDICINALS AT THE ÉCOLE SUPÉRIEURE DE PHARMACIE
Vauquelin was the director of this school from the time of its reorganization in 1803 until his death in 1829.

The fact that the zinc carbonate could not be converted into the oxide without discoloration interested Dr. Stromeyer greatly:

> This information [said he] induced me to examine the oxide of zinc more carefully, and I found, to my great surprise, that the colour which it assumed was owing to the presence of a peculiar metallic oxide, the existence of which had not hitherto been suspected. I succeeded by a peculiar process in freeing it from oxide of zinc, and in reducing it to the metallic state . . . . (*10*).

His method of obtaining the metal was as follows. He dissolved the impure zinc oxide in sulfuric acid and passed in hydrogen sulfide. After filtering and washing the precipitate of mixed sulfides, he dissolved it in concentrated hydrochloric acid and evaporated to dryness to drive off excess acid. After dissolving the residue in water, he added a sufficient excess of ammonium carbonate solution to redissolve any zinc and copper that may have been precipitated. Since the carbonate of the new element was not soluble in excess ammonium carbonate, Dr. Stromeyer filtered it off, washed it, and ignited it to the oxide. After mixing the brown oxide with lampblack in a glass or earthen retort, he heated the mixture to moderate redness. Upon opening the retort he found a bluish gray metal with a bright luster (*10*).

However, since he had only three grams of the new metal, he was unable at first to make a thorough study of its properties. Fortunately, he soon received more of it from an unexpected source, for in the same letter to Dr. Schweigger he wrote:

> I am happy, therefore, to be able to inform you, that within these few days, through Mr. Hermann, of Schönebeck, and Dr. Roloff, of Magdeburg, who took an interest in this metal, I have been placed in a situation which will enable me to carry my experiments further. During the apothecary's visitation in the state of Magdeburg some years ago, there was found in the possession of several apothecaries, a preparation of zinc from Silesia, made in Hermann's manufactory at Schönebeck, which was confiscated on the supposition that it contained arsenic, because, when dissolved in acids, and mixed with sulphuretted hydrogen, it let fall a yellow precipitate, which, from the chemical experiments made on it, was considered as orpiment.
>
> This fact [continued Stromeyer] could not be indifferent to Mr. Hermann, as it affected the credit of his manufactory, and the more especially as the Medicinal Counsellor Roloff, who had assisted at the Apothecaries' visitation, had drawn up a statement of the whole, and sent it to Hufeland, who published it in the February number of his *Medical Journal*. He, therefore, subjected the suspected oxide of zinc to a careful examination; but he could not succeed in detecting any arsenic in it (*24*).
>
> He then requested the Medical Counsellor Roloff (*23*) to repeat his experiments on the oxide once more. This he did very readily and he now perceived that the precipitate which had at first been taken by him for orpiment, was not so in reality; but owed its existence to the presence of another metal, having considerable resemblance to arsenic, but probably new. To obtain full certainty on the subject, both the gentlemen* had recourse to me, and have sent me, within these few days, both a portion of the Silesian oxide of zinc and specimens of the orpiment-like precipitate and of the metal extracted from it, with the request that I would subject these bodies to a new examination, and in particular that I should endeavour to ascertain whether they contained any arsenic (*10*).

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* Dr. Roloff (*31*) explained that this was not done to settle a dispute.

Dr. Stromeyer soon surmised that the metal which Mr. Hermann and Dr. Roloff had extracted from the Silesian zinc oxide was the same as the one he had obtained from the Salzgitter product (*31*), (*35*), (*39*):

> From the particulars already stated [said he] I considered it as probable that this Silesian oxide of zinc contained likewise the metal which I had discovered; and as it gives with sulphuretted hydrogen a precipitate similar in colour to orpiment, I considered this to be the reason why the oxide was supposed to contain arsenic. Some experiments made upon it fully confirmed this opinion. I have, therefore, informed Mr. Hermann of the circumstance by the post; and I shall not fail to give the same information to Medicinal Counsellor Roloff, whose letter I received only the day before yesterday.

This discovery gave great satisfaction and relief to Mr. Hermann because it again brought his pharmaceutical establishment into good standing, and it also gave Dr. Stromeyer the opportunity to make a more thorough study of the new metal and its compounds. Because this metal is so frequently found associated with zinc, he named it *cadmium*, meaning *cadmium fornacum* or *furnace calamine*. In the researches which led to this discovery, he was assisted by two of his students, Mr. Mahner of Brunswick and Mr. Siemens of Hamburg.

W. Meissner (*36*) of Halle and C. Karsten (*25*) of Berlin, without any knowledge of the work done by Stromeyer, Roloff, and Hermann, also discovered cadmium independently (*11*). Meissner analyzed two products from the Schönebeck plant sent him by Superintendent of Mines von Veltheim, one of which proved to be the carbonate and the other the sulfide of the new metal. By dissolving the carbonate in nitric acid and placing a rod of pure zinc in the solution, he obtained a voluminous, light gray deposit. When he washed and dried it and ground the resulting powder in an agate mortar, it exhibited a metallic luster. Meissner made a careful study of the metal and its compounds.

In 1817, perhaps as a result of his great discovery, Dr. Stromeyer received the honorary title of *Hofrath*, or court counselor. After publishing many papers on mineralogy and chemistry, and serving his university for many years as an inspiring teacher, he died on August 18, 1835, in the city where he was born and where he had spent most of his life (*8*).

In 1821 Nils Nordenskiöld wrote to Berzelius, "Stromeijer [sic] has the finest and neatest laboratory I have yet seen in Germany, and is certainly one of the few whose analyses are somewhat reliable. Nevertheless his procedures differ from yours in many important respects. I shall take the liberty of mentioning a few of the differences I have noticed. One sees no filter stand. All filtrations are made in glass cylinders such as come with our brandy gauges, one foot high and from 3 to 1 inch in diameter; as the funnels are wider, they are simply placed over the edge of the glass, the liquid spatters around, but the filter takes up that which spatters out.

The filter is folded like the French ones and always extends over the rim of the funnel. The filter is not burned. The solutions are also precipitated in the above-mentioned glass cylinders, and the digestions are made in retorts or small flasks with long necks and thin bottoms. The sandbath is not used; the heating is done over the free flame or on hot plates. In regard to reagents, I have noticed that he prefers to use the fixed alkalies as precipitating agents instead of ammonium hydroxide, which I believe involves difficulty in washing the filter, especially such as they use here. The balance Stromeyer uses is very good, but one has to walk through a hall to reach the room where it is kept" (*61*).

An important application of the cold light from certain compounds of zinc, cadmium, and other elements of Group II of the periodic system is the modern fluorescent lamp. A long tube, containing an inert gas at low pressure and a few droplets of mercury, is constructed with an electrode at each end. This tube has an inside coating of some stable, fluorescent substance which will absorb the resonance line of a low pressure mercury discharge in the ultraviolet at 2,537 Ångström units and re-radiate this energy in a desirable part of the visible spectrum (*57*). The basic part of the fluorescent compound used always contains a lower atomic weight metal from Group II. Zinc silicate, for example, gives a green fluorescence; cadmium silicate and the borates of cadmium and zinc give pink; magnesium tungstate and zinc beryllium silicate give white light; and calcium tungstate gives blue.

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XVIII. SOME ELEMENTS ISOLATED WITH THE AID OF POTASSIUM AND SODIUM: ZIRCONIUM, TITANIUM, CERIUM, AND THORIUM

The earths of the titanium group had a cosmopolitan origin. The German chemist Klaproth discovered zirconia in 1789 while analyzing a zircon from Ceylon. Two years later the English clergyman William Gregor found titania, or "menachanite," in a black sand from his own parish in Cornwall, but announced his discovery in such a modest manner that it made little impression on the scientific world. Klaproth rediscovered this earth four years later in a Hungarian red schorl, and named it "Titanerde," or titania. Hisinger and Berzelius discovered ceria in 1803 while investigating the Swedish mineral "heavy stone of Bastnäs," now known as cerite. Berzelius found thoria, the last of these earths, in 1829 in a specimen of thorite that had been sent to him from an island off the coast of Norway. The difficult isolation of the metals titanium, cerium, zirconium, and thorium was accomplished by various methods involving the powerful reducing action of sodium and potassium.

. . . . . .

> *Es hat wohl nie eine Wissenschaft, in einem kleinern Zeitraume, raschere Fortschritte gemacht, als die chemische Naturkenntniss (1)*.*

Zirconium

Zirconium minerals are widely distributed in Nature, and have been used for centuries. In his enraptured description of the four-square city, Saint John the Divine mentioned the jacinth (or hyacinth) as one of the twelve precious stones that garnished the foundations of the city wall (*14*).

Although zircon was frequently used by the ancients for intagli, and although hyacinth and jargon were well known in the Middle Ages, the presence in these minerals of an unknown metal was not suspected until near the end of the eighteenth century. The earth zirconia was overlooked because of its great similarity to alumina, and it took the analytical skill of a Klaproth to detect it. In 1789 he analyzed a specimen of zircon from Ceylon, and realized that it contained a large quantity of a new earth, which he named *Zirconerde*, or, as one says in English, *zirconia* (*9*), (*31*), (*32*). All analyses of zirconium minerals made before the discovery of this earth were incorrect. The celebrated Torbern Bergman had, for example, reported the following composition for a certain hyacinth from Ceylon:

Silica	*Alumina*	*Iron Oxide*	*Lime*
25%	40%	13%	20%

When Klaproth analyzed the same specimen he found:

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* "No science has ever made more rapid progress in a shorter time than chemistry,"

Silica	*Iron Oxide*	*Zirconia (Jargonia)*
25%	0.5%	70%

His results were soon confirmed by Guyton Morveau* and by Vauquelin (*9*), (*33*), (*34*), (*35*). This mineral is now known to be zirconium silicate, $ZrSiO_4$.

In 1808 Sir Humphry Davy tried in vain to decompose zirconia with the electric current, but Berzelius (*36*) finally obtained the metal in 1824 by heating a dry mixture of potassium and potassium zirconium fluoride in a very small closed iron tube placed inside a platinum crucible. After the quiet reaction had taken place, he cooled the tube and placed it in distilled water, whereupon, to use his own words, "There fell from the tube a black powder as fast as the salt dissolved, and at the same time there was evolved a small quantity of hydrogen. . . . The zirconium obtained in this manner is easily deposited. It can be washed with water without oxidizing. Washed and dried, it forms a black powder resembling charcoal, which cannot be compressed nor polished like a metal" (*15*).

GUYTON-MORVEAU
1737–1816

French attorney and chemist. Professor of chemistry at the École Polytechnique from 1794 to 1815. With Lavoisier, Fourcroy, and Berthollet he brought chemical nomenclature into accord with modern views on combustion. He made the first serious researches on the structure of steel.

Although Berzelius' method yielded impure zirconium, highly contaminated with zirconia, he had chosen his materials with great scientific acumen (*37*). Through the attempts of many research workers, including Ludwig Weiss and Eugen Naumann (*38*), Wedekind (*39*), and Moissan (*40*), zirconium of higher and higher purity has been obtained. Finally in 1914 D. Lely, Jr., and L. Hamburger (*41*) of the research staff of the Philips Metal-Incandescent Lamp Works in Eindhoven, Holland, obtained the metal 100% pure. Their method consisted in heating a mixture of the tetrachloride and sodium in a bomb, using the electric current as the source of heat. The metal consisted of laminae which could be pressed into rods, drawn into wire, or burnished to a bright, mirror-like surface.

The element is still best known, however, in the form of its oxide. Zirconia linings for metallurgical furnaces are very permanent, and, because of their low heat conductivity, may be made very thin. Zirconia refractories, such as crucibles, are very resistant to the action of heat, slags, and

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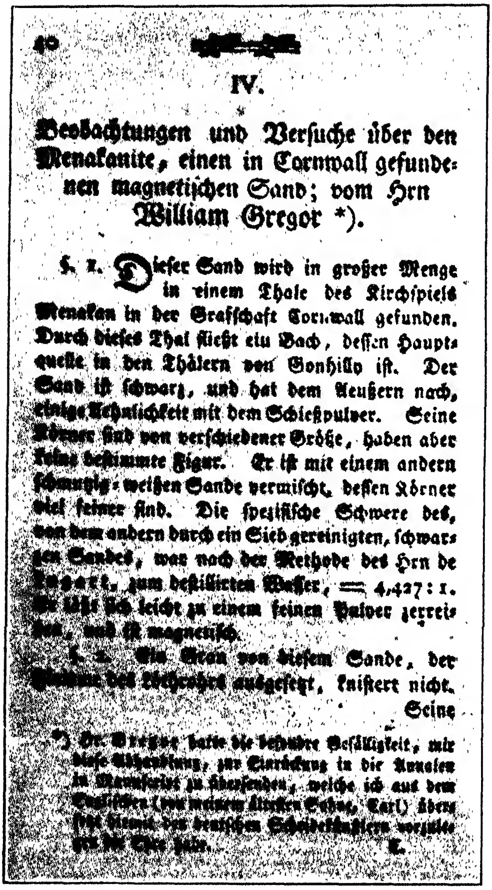
* During the Revolution, the scientific papers of Morveau were signed "Cit[oyen] Guyton."

most acids, and may safely be plunged into water while red-hot (*42*).

Titanium

Joseph Priestley was not the only English clergyman to discover a new element. The Reverend William Gregor met with similar good fortune. He was born in 1761 in Cornwall, and was educated for the ministry at Bristol and Cambridge, where he made an excellent scholastic record, especially in mathematics and the classics. He held pastorates at Deptford near Totness, at Bratton Clovelly in Devonshire, and finally at Creed near Grampound, Cornwall (*2*).



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IV.

Beobachtungen und Verſuche über den Menakanite, einen in Cornwall gefundenen magnetiſchen Sand; vom Hrn William Gregor *).

§. 1. Dieſer Sand wird in großer Menge in einem Thale des Kirchſpiels Menakan in der Grafſchaft Cornwall gefunden. Durch dieſes Thal fließt ein Bach, deſſen Hauptquelle in den Thälern von Gonhilly iſt. Der Sand iſt ſchwarz, und hat dem Aeußern nach, einige Aehnlichkeit mit dem Schießpulver. Seine Körner ſind von verſchiedener Größe, haben aber keine beſtimmte Figur. Er iſt mit einem andern ſchmutzig-weißen Sande vermiſcht, deſſen Körner viel feiner ſind. Die ſpezifiſche Schwere des, von dem andern durch ein Sieb gereinigten, ſchwarzen Sandes, war nach der Methode des Hrn de Saussure, zum deſtillirten Waſſer, = 4,427 : 1. Er läßt ſich leicht zu einem feinen Pulver zerreiben, und iſt magnetiſch.

§. 2. Ein Gran von dieſem Sande, der Flamme des Löthrohrs ausgeſetzt, kniſtert nicht.

Seine

*) Hr. Gregor hatte die beſondre Gefälligkeit, mir dieſe Abhandlung, zur Einrückung in die Annalen im Manuſcripte zu überſenden, welche ich aus dem Engliſchen (von meinem älteſten Sohne, Carl) überſetzt hiemit den deutſchen Scheidekünſtlern vorzulegen die Ehre habe. C.

INTRODUCTION TO THE REVEREND WILLIAM GREGOR'S ORIGINAL PAPER ON TITANIUM, OR "MENACHANITE." *Crell's Annalen*, 1791

He became intensely interested in the minerals of England, and acquired such great skill in analyzing them that Berzelius and other competent judges referred to him as "a famous mineralogist" (*3*). He was a founder and honorary member of the Royal Geological Society of Cornwall, and his analyses of such substances as bismuth carbonate, topaz, wavellite, uranium mica (Uranglimmer) (*16*), and native lead arsenate (*17*) were of high excellence (*4*).

The most interesting mineral that Mr. Gregor ever analyzed, however, was a black, magnetic sand from the Menachan valley in his own parish. His account of this analysis, as it appeared in *Crell's Annalen* in 1791, was introduced by the following editorial note:

> Mr. Gregor did me the special favor of sending the manuscript of this paper for insertion in the *Annalen*, the translation of which from the English by my eldest son Carl, I have the honor to present to German analytical chemists.

The paper begins with a minute description of the sand:

> This sand [said Mr. Gregor] is found in large quantity in a valley of the Menachan parish in the county of Cornwall. Through this valley there flows a stream whose principal source is in the valleys of Gonhilly. The sand is black, and in external appearance resembles gunpowder. Its grains are of various sizes, but have no definite shape. It is mixed with another dirty-white sand, the grains of which are much finer. . . . .

Gregor found that the black portion of this sand had the following composition:

Magnetite	*Silica*	*Reddish Brown Calx*	*Loss*
$46^{9}/_{16}\%$	$3^{1}/_{2}\%$	45%	$4^{15}/_{16}\%$

The "reddish brown calx" dissolved in sulfuric acid to give a yellow solution which became purple when reduced with zinc, tin, or iron, and when the pulverized mineral was fused with powdered charcoal, a purple slag was formed.

Mr. Gregor modestly stated that his paper was not a complete investigation, but merely a record of disconnected facts, the interpretation of which he would leave to more skilful workers and keener philosophers than himself. His friend, John Hawkins, to whom he showed the black sand, agreed that it must be a new mineral.

The Edgar Fahs Smith Memorial Collection, University of Pennsylvania

D. LORENTZ VON CRELL
1744–1816

Editor of *Chemische Annalen für die Freunde der Naturlehre, Arzneigelahrtheit, Haushaltungskunst und Manufakturen* and of Crell's *Neues Chemisches Archiv*. Professor of chemistry and counselor of mines at Helmstädt.

> The opinion of a man so distinguished in mineralogy [said Mr. Gregor], together with the extraordinary properties of the sand, led me to believe that it must contain a new metallic substance. In order to distinguish it from others, I have ventured to give it a name derived from the region where it was found—namely, the Menachan parish—and therefore the metal might be called menachanite.

He cautiously added that perhaps the researches of other chemists might some day explain the unusual properties of the mineral and "rob it of its novelty." His many duties unfortunately prevented him from continuing the investigation (*5*) of this black magnetic sand now known as ilmenite, $FeTiO_3$. Strangely enough, his announcement did not attract much attention, and thus titanium, like tellurium, was quickly forgotten.

William Gregor died at Creed in the summer of 1817, after prolonged suffering with tuberculosis (*47*). Thomas Thomson once said of him:

> Mr. Gregor of Cornwall was an accurate man, and attended only to analytical chemistry; his analyses were not numerous, but they were in general excellent. Unfortunately the science was deprived of his services by a premature death (*6*).

Mr. Gregor's intimate friend, the Reverend J. Trist of Veryan, mentioned the exemplary manner in which he had fulfilled all the duties of his Christian pastorate, "dispensing to his neighbors both spiritual and temporal benefits, and enlivening the society of his friends by his cheerful and instructive conversation" (*2*).

MARTIN HEINRICH KLAPROTH
1743–1817

German analytical chemist. First professor of chemistry at the University of Berlin. In 1810 he published, with F. Wolff, a chemical dictionary containing references to the researches cited therein. Klaproth's six-volume "*Beiträge zur chemischen Kenntniss der Mineralkörper*" is a collection of his remarkable mineral analyses. He rediscovered Gregor's "*menachanite,*" made a thorough study of its properties, and rechristened it *titanium.*

The reader will recall how the honored chemist, Martin Heinrich Klaproth, resurrected tellurium, giving full credit to the original discoverer, Müller von Reichenstein. After Mr. Gregor's discovery had likewise fallen into oblivion, Klaproth again came to the rescue. In 1795 he separated what seemed to be a new oxide from a specimen of red schorl, or rutile, found in Boinik, Hungary, and presented to him by Count Würben of Vienna (*7*), (*8*). However, since this oxide bore such a close resemblance to the one previously described by Mr. Gregor, Klaproth analyzed a specimen of menachanite, or "iron-shot titanite from Cornwall," as he preferred to call it, for comparison (*21*):

> Within a few years [said he] a fossil has been brought into notice by the name of *Menachanite,* which has been found in the parish of *Menachan,* in *Cornwall,* and consists of grey-black, sand-like grains, obeying the magnet. Mr. M'Gregor, of Menachan, who dedicates his study to mineralogical chemistry, has given not only the first information of this fossil, but also a full narrative of his chemical researches concerning it. The chief result of these is, that menachanite has for its constituent parts iron, and a peculiar *metallic oxyd of an unknown nature.* By the following examination it will appear that this substance, which, besides iron, forms the second chief component principle of menachanite, is precisely the very same which constitutes the Hungarian red schörl; namely, *oxyd of titanium.* With this opinion also, most of the phenomena noted down by M'Gregor, in his operations with menachanite, agree.

Klaproth gave the following curious reason for preferring to call the new element titanium:

> Whenever [said he] no name can be found for a new fossil which indicates its peculiar and characteristic properties (in which situation I find myself at present), I think it best to choose such a denomination as means nothing of itself, and thus can give no rise to any erroneous ideas. In consequence of this, as I did in the case of uranium, I shall borrow the name for this metallic substance from mythology, and in particular from the Titans, the first sons of the earth. I therefore call this new metallic genus TITANIUM (*8*), (*9*).

Klaproth, Vauquelin, Heinrich Rose (*22*), and others tried in vain to isolate the metal. In 1822 Dr. Wollaston thought he had found it in the form of minute cubic crystals in the slag of the iron works at Merthyr Tydvil, but Wöhler (*18*) showed in 1849 that these were not the metal itself but a mixture of the nitride and cyanide. In 1825 Berzelius (*20*) prepared some very impure amorphous titanium by reducing potassium fluotitanate, K_2TiF_6, with potassium. Although the resulting black powder gave a metallic streak, it was insoluble in hydrofluoric acid and therefore could not have contained much titanium metal (*23*).

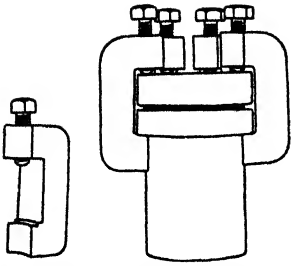
In 1849 Wöhler and Deville attempted to prepare pure titanium by Berzelius' method, but used a closed crucible in order to exclude air. When they found that the product thus obtained still contained titanium nitride, they heated boats containing potassium and potassium fluotitanate in an atmosphere of hydrogen and obtained a gray powder which showed a metallic luster when examined with a microscope (*7*), (*10*), (*18*). Wöhler and Deville thought they had the metal, but, in the opinion of W. M. Thornton, Jr. (*23*), they were still dealing with the nitride.

SVEN OTTO PETTERSSON
1848–1941

Professor of chemistry at the University of Stockholm from 1881–1908. He collaborated with Lars Fredrik Nilson in researches on metallic titanium and the physical constants of titanium and germanium. He was one of the first chemists to support Arrhenius in his views on electrolytic dissociation.

In 1887 Lars Fredrik Nilson and Otto Pettersson finally prepared the metal 95 per cent pure by reducing the tetrachloride with sodium in an air-tight steel cylinder (*24*), (*48*). The titanium that Moissan obtained from his electric furnace was free from nitrogen and silicon and contained only 2 per cent of carbon (*25*).

In 1910 M. A. Hunter (*26*) obtained the metal 99.9 per cent pure by a modification of Nilson and Pettersson's method in which pure titanic chloride and sodium were heated in a 1000-cc. machine steel bomb capable of bearing 40,000 kilograms of pressure. The lid, which rested on an intervening gasket of soft copper, was securely held in place by six braces. After the temperature had been raised to low redness, the reaction took place quickly and violently. The sodium chloride was then leached out with water, leaving the pure titanium.



Rensselaer Polytechnic Institute, Eng. Sci. Series, No. 1, p. 6 (1911)

M. A. HUNTER'S BOMB FOR PREPARING METALLIC TITANIUM

The oxide titania, TiO_2, because of its high refractive index, is used in high-grade white pigments of great opacity and covering power. The metal unites with iron to form the useful alloy, ferro-titanium, which is added to molten steel to prevent formation of air bubbles, which would form holes in the finished castings. Thus the element that lay hidden for centuries in the sand of Mr. Gregor's parish is now of direct benefit to mankind.

Cerium

Wilhelm Hising, or Hisinger as he was called after being raised to the nobility, belonged to a wealthy Swedish family that owned the famous Riddarhyttan* property in Vestmanland and the Bastnäs mine, in which the mineral cerite was discovered. He was born in December, 1766, and soon learned to love the beautiful minerals of Sweden. When only fifteen years old he sent some cerite to the famous Scheele for analysis, and the reply showed that even the greatest of men sometimes make mistakes.

STATUE OF CARL WILHELM SCHEELE AT KÖPING, SWEDEN

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* The reader will recall that Riddarhyttan was also the birthplace of Georg Brandt, the discoverer of cobalt.

Scheele reported that he was unable to discover any new metal in the cerite However, as Baron Nordenskiöld said, this mistake is very excusable, for the mineral is difficult to handle even with modern methods of analysis (*11*).

Berzelius described cerite as follows:

> In the iron mine at Bastnäs, now abandoned, in the vicinity of Vestmanland, one finds a mineral of exceedingly high specific gravity, called "heavy stone of Bastnäs"; that is why Scheele searched there, but in vain, for tungsten. This mineral remained in oblivion until 1803, when it was simultaneously examined by Klaproth (*44*), by Hisinger and by myself (*29*). We found in it a new substance; Klaproth called it terre ochroite. Hisinger and I called it cerous oxide, because there is a higher oxide, and the two oxides give salts of different colors and properties. The root of the name cerium was deduced from that of Ceres,† which Klaproth changed to cererium, but this name was soon abandoned. The mineral is composed mainly of cerous silicate, and for this reason receives the name of cerite. Cerium was afterward discovered in minerals from other localities; for example, in gadolinite, orthite, allanite, yttrocerite, cerous fluoride, etc." (*12*).

The main object of Berzelius and Hisinger's analysis of cerite was to search for yttria, which might easily have escaped the attention of Scheele and d'Elhuyar since it was unknown at the time their investigation was made (*29*). Although they failed to find yttria, Berzelius and Hisinger discovered instead the new earth ceria.§

Medallion by Kjellberg

AXEL FREDRIK CRONSTEDT*
1722–1765

Swedish chemist and mineralogist. Discoverer of nickel. Author of a "System of Mineralogy" which was translated into several languages. He called the heavy mineral now known as *cerite* "*tungstein of Bastnäs.*" Hence Scheele thought it might contain tungsten.

In his "Early Recollections of a Chemist," Wöhler gives a charming picture of Hisinger's home:

> After a five days' stay at Fahlun [he writes] we drove to Skinnskatteberg, Hisinger's estate, where, after a drive of twenty-four hours, we

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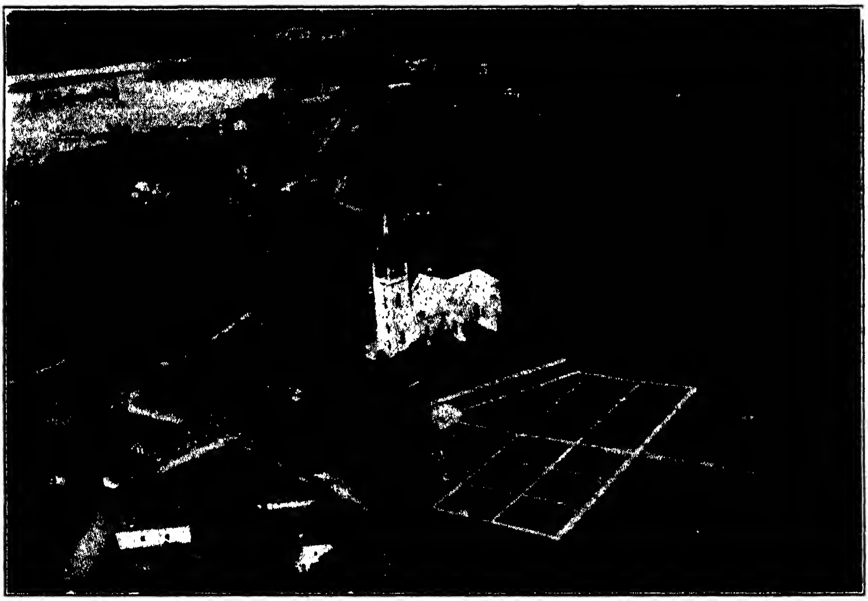
* See Part IV, pp. 70–3, for biographical sketch.

† The element was named for the planet Ceres, which had been recently discovered by Piazzi.

§ In volumes 9 and 10 of *Nicholson's Journal* this paper was accredited to W. D'Hesinger and J. B. Bergelius (*sic!*).

> arrived one afternoon, finding Berzelius there. The venerable, genial, and most original Hisinger, so well known through his contributions to the geognostic mineralogy and botany of Sweden, and through the liberality with which he had supported Berzelius during the commencement of his studies, lived here a very rich man (Brukspatron) on a princely estate, surrounded by magnificent forests, gardens, and iron mines. We spent a week here most delightfully, partly occupied in examining his collections, with making blowpipe tests of unknown minerals, and with the reading aloud of my translation of Hisinger's "Mineral Geography." In company with Berzelius and Hisinger, we made an excursion a few miles distant to the mines of Riddarhyttan, among which the Bastnäshaft is known as the only locality for the occurrence of cerite. At the mouth of this mine, which at that time had already been abandoned, we collected in the scorching sun hundreds of the most characteristic specimens of cerite and cerin [allanite] (*13*).

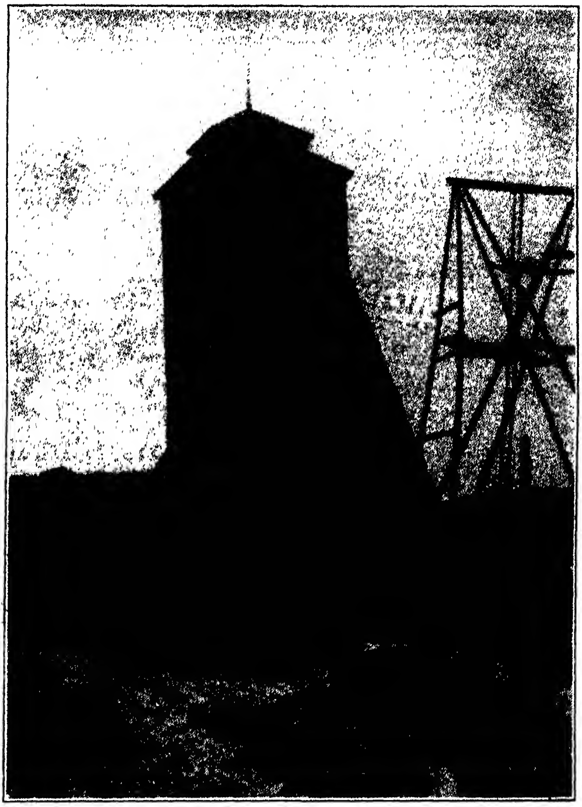


SKINNSKATTEBERG, VESTMANLAND, SWEDEN, WHERE WILHELM HISINGER USED TO LIVE

The mineral cerite was first found in one of the mines on his estate.

Hisinger was indeed one of Sweden's most eminent mineralogists and geologists. He died on June 28, 1852, at the venerable age of eighty-five years.

Gahn in Sweden and Vauquelin in France tried in vain to obtain metallic cerium. Mosander prepared anhydrous cerous chloride and subjected it for a long time to the action of potassium vapor. After washing the residue with cold alcohol, he obtained a brown powder which, when burnished, exhibited a dark metallic luster. This cerium was far from pure, however, for it was badly contaminated with the oxychloride. Impure cerium was also prepared by Wöhler. Hillebrand and Norton (*27*) succeeded in 1875 in preparing the metal in a coherent form by electrolyzing fused cerous chloride. In 1911 the late Dr. Alcan Hirsch (*30*) made some electrolytic cerium containing only two per cent of impurities (iron, cerium oxide, and cerium carbide). The metal was purified by amalgamating it and distilling off the mercury in an evacuated quartz tube lined with magnesia. This elaborate investigation required more than three years of work at the University of Wisconsin.



From "Industry in Sweden," Federation of Swedish Industries

MINE HEAD-FRAME AT RIDDARHYTTAN

The mineral cerite was discovered there in 1781 by Wilhelm von Hisinger. Georg Brandt, the discoverer of cobalt, was born at Riddarhyttan.

Cerium forms with iron a peculiar pyrophoric alloy which, when struck, emits showers of sparks, and which is used somewhat in the manufacture of automatic gas-lighters (*28*).

Thorium

While analyzing one of the rare minerals from the Fahlun district, Berzelius found in 1815 a substance that he believed to be the oxide of a new metal which he named thorium in honor of the ancient Scandinavian god, Thor. Ten years later he himself found that this substance was not a new earth, but simply yttrium phosphate. He evidently liked the name thorium, however, for when in 1829 he really did discover a new element, he christened it with the same name (*45*).

WILLIAM FRANCIS HILLEBRAND*
1853–1925

Chemist with the U. S. Geological Survey, later Chief Chemist at the Bureau of Standards. President of the American Chemical Society in 1906. Author of "The Analysis of Silicate and Carbonate Rocks." He was the first to suggest the possibility of recovering potash from the fumes from cement kilns.

In his account of the discovery, Berzelius wrote:

> The mineral on which I made the following experiments is found in the syenite on the island of Lövö near Brevig, Norway. It was discovered by the pastor Esmarck, son of Jens Esmarck, famous professor at the University of Christiania. It is the latter who sent me a specimen, asking me to examine it, because, on account of its high specific gravity, he believed it to be the earth of tantalum. This mineral is black, with no indication of crystalline form or texture, and looks exactly like gadolinite from Ytterby; the exterior presents sometimes a thin rust-colored surface layer (*12*).

This mineral, which is now known as thorite, consists essentially of thorium silicate, $ThSiO_4$ (*50*).

Thorium, like the other metals of this group, is isolated with great difficulty. Berzelius prepared the impure metal by heating a mixture of potassium and potassium thorium fluoride in a glass tube. D. Lely, Jr., and L. Hamburger prepared it

THOMAS H. NORTON†
1851–1941

Professor of chemistry at the University of Cincinnati. American consul at Harput, Turkey, at Smyrna, and at Chemnitz, Saxony. Author of books on dyes, the cottonseed industry, potash production, and the utilization of atmospheric nitrogen. Collaborator with W. F. Hillebrand in researches on cerium (*46*), (*49*).

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* See ALLEN, "Pen Portrait of William Francis Hillebrand, 1853–1925," J. CHEM. EDUC., 9, 72–83 (Jan., 1932).

† See *Ind. Eng. Chem., News Ed.*, 13, 318–9 (Aug. 10, 1935).

99 per cent pure by distilling sodium and thorium chloride into an exhausted steel cylinder and also succeeded in obtaining it as a coherent metal (*9*), (*41*). It is interesting to note that all four of the elements of this group, titanium, cerium, zirconium, and thorium, were isolated with the aid of the alkali metals discovered by Sir Humphry Davy.

In 1898 Mme. Curie in Paris and Professor G. C. Schmidt at the University of Münster, working independently, found that thorium, like uranium, is radioactive (*43*). This discovery opened up a vast new field of research as a result of which thorium is now known to be the parent substance of an entire series of radioactive elements. The story of their discovery will be reserved, however, for a later chapter.


W. Hisinger

From Söderbaum's Jac. Berzelius Brev

WILHELM HISINGER
1766–1852

Swedish mineralogist and geologist. Owner of the famous Riddarhytta mining property in Vestmanland, where cerite was discovered. He was one of the first to analyze the lithium mineral petalite.

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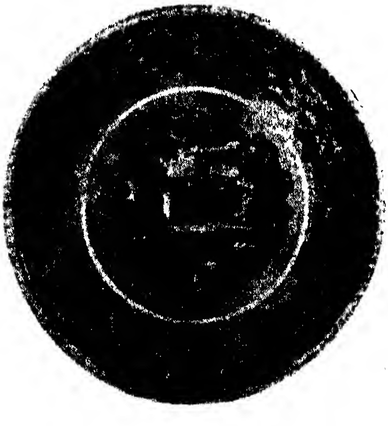

XIX. OTHER ELEMENTS ISOLATED WITH THE AID OF POTASSIUM AND SODIUM: BERYLLIUM, BORON, SILICON, AND ALUMINUM

When the Abbé Haüy pointed out the close similarity and probable identity of beryl and the emerald, Vauquelin analyzed them carefully, and found in 1798 that they are indeed identical, and that they contain a new earth, which he named glucina, but which is now known as beryllia. The metal was isolated thirty years later by Wöhler and Bussy independently. Boron was isolated in 1808 by Gay-Lussac and Thenard in France and by Davy in England by reduction of boric acid with potassium. Although amorphous silicon was prepared by Berzelius in 1824, the crystalline form of it was not obtained until about thirty years later, when Henri Sainte-Claire Deville prepared it by an electrolytic method. Aluminum was isolated in 1825 by the Danish physicist, Oersted, and two years later Wöhler prepared it by a better method. Successful commercial processes for the manufacture of this important metal were perfected by Henri Sainte-Claire Deville, by Charles Martin Hall, and by Dr. Paul L. T. Héroult.

. . . .

> *Aber neue Phaenomena zu erklären, dieses macht meine Sorgen aus, und wie froh ist der Forscher, wenn er das so fleissig Gesuchte findet, eine Ergötzung wobei das Herz lacht (1).**

Beryllium

Pliny the Elder realized that beryl and the emerald are closely related (*56*). In speaking of the discovery of beryllium Fourcroy once said, "It is to geometry that we owe in some sort the source of this discovery; it is that [science] that furnished the first idea of it, and we may say that without it the knowledge of this new earth would not have been acquired for a long time, since according to the analysis of the emerald by M. Klaproth and that of beryl by M. Bindheim one would not have thought it possible to recommence this work without the strong analogies or even almost perfect identity that Citizen Haüy found for the geometrical properties between these two stony fossils" (*5*).

As a result of his analysis of a Peruvian emerald, Klaproth had stated that this gem has the following composition:

Silica "silex"	*Alumina, "alumine or argil"*	*Iron oxide*
66.25%	31.25%	0.50%

To explain his extravagance he said, "For the specimen of emerald sacrificed to this analytical process, I am indebted to the liberal kindness of Prince Dimitri Gallitzin, whose zeal for the study of mineralogy is most honourably known" (*22*).

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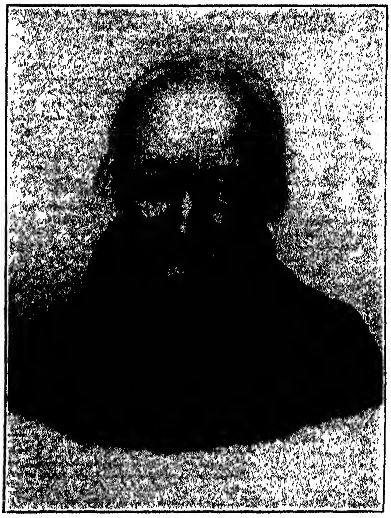
* For a translation of this quotation see page 101.



From "La Science Française," Dept. Public Instruction, Paris

RENÉ-JUST HAÜY
1743–1822

French mineralogist. He deduced the fundamental laws of crystallography, and explained cleavage by postulating that a crystal is built up of small similar parallelopipeds. He was the first to recognize that beryl and the emerald are geometrically identical. Vauquelin's proof of their chemical identity, made at the suggestion of Haüy, led to the discovery of the element beryllium.

Beryl had also been analyzed by Bergman, Achard, Bindheim, and Vauquelin, and was supposed to be a calcium aluminum silicate (*23*). The identity of beryl and the emerald was not suspected until the famous French mineralogist, the Abbé Haüy, made a careful study of their crystal forms and physical properties and was so struck by the similarity of the two minerals that he asked Vauquelin to analyze them chemically.

Although the latter had previously overlooked the new earth because of its similarity to alumina, he found in 1798 that the hydroxide that precipitates when caustic potash is added to an acid solution of the beryl does not dissolve in an excess of the alkali. It also differs from alumina in other respects, for it forms no alum, it dissolves in ammonium carbonate, and its salts have a sweet taste. Vauquelin's paper read before the French Academy on "le 26 pluviose an VI" of the Revolutionary Calendar, or the fifteenth of February, 1798 (*6*), (*23*), proved that, except for a little chromium in the emerald, the two gems have the same composition and that they contain a new earth, a sample of which he presented to the Academy. At the suggestion of the editors* of the *Annales de Chimie et de Physique*, he called the new earth *glucina*, meaning *sweet*. The specimen of beryl that Vauquelin analyzed was presented to him by "Citizen Patrin, whose zeal for the advancement of the sciences is well known to every one of their cultivators" (*23*).

Vauquelin believed that Bergman's incorrect conclusions as to the chemical nature of the beryl had been caused by the unwillingness of his "active mind to submit to the details of experiment." Thus Bergman, and Bindheim as well, had entrusted their analyses to young pupils who were incapable of distinguishing a new substance when they saw it. According to Bindheim's analysis, the beryl consisted of 64 per cent of silica, 27 per cent of alumina, 8 per cent of lime, and 2 per cent of iron (total 101 per cent) (*23*).

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* Guyton-Morveau, Monge, Berthollet, Fourcroy, Seguin, Chaptal, and Vauquelin.

JOHANN FRIEDRICH GMELIN
1748–1804

Father of Leopold Gmelin. Professor of chemistry at Tübingen and Göttingen. Famous chemical historian. His remarkable *"Geschichte der Chemie"* was published in 1797–99.

When Vauquelin analyzed a Peruvian emerald (*25*) after his discovery of chromium and glucina, the results differed greatly from his previous ones and from those of Klaproth. He found:

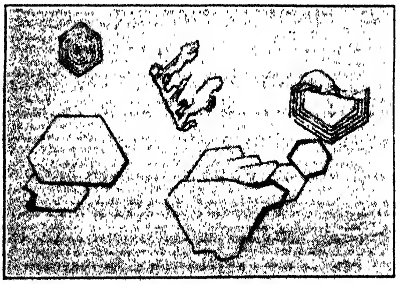
Silica	64.60
Alumina	14.00
Glucina	13.00
Lime	2.56
Chromium oxide	3.50
Moisture, or other volatile matter	2.00
	99.66

J. F. Gmelin's analysis of a Siberian beryl soon confirmed Vauquelin's conclusions as to the essential constituents of that gem, for he found no lime, but only silica, alumina, glucina, and a small amount of iron oxide (*26*).

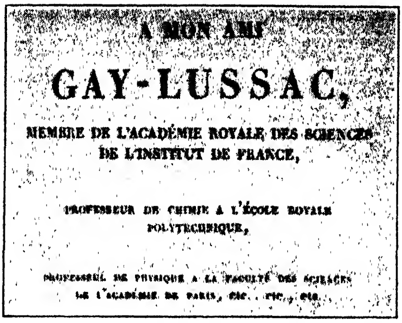
Since yttria, as well as glucina, forms sweet salts, Klaproth preferred to call the latter earth beryllia, and it is still known by that name. Beryl and the emerald are now known to be a beryllium aluminum silicate [$Be_3Al_2(SiO_3)_6$].

Metallic beryllium was first prepared in August, 1828, by Wöhler and Bussy independently by the action of potassium on beryllium chloride (*7*), (*8*). Wöhler placed alternate layers of the chloride and flattened pieces of potassium in a platinum crucible, wired the cover on strongly, and heated the mixture with an alcohol lamp. The reaction began immediately and took place with such intensity that the crucible became white-hot. After cooling it thoroughly, he opened it and placed it in a large volume of water, whereupon the beryllium separated out as a gray-black powder. After washing this insoluble material, Wöhler saw that it consisted of fine metallic particles which could be burnished to show a dark metallic luster. He did not succeed in melting the beryllium (*8*).

The first person to prepare pure beryllium by an electrolytic process was



HEXAGONAL CRYSTALS OF PURE BERYLLIUM PREPARED BY P. LEBEAU



A MON AMI
GAY-LUSSAC,
MEMBRE DE L'ACADÉMIE ROYALE DES SCIENCES
DE L'INSTITUT DE FRANCE,

PROFESSEUR DE CHIMIE A L'ÉCOLE ROYALE
POLYTECHNIQUE,

PROFESSEUR DE PHYSIQUE A LA FACULTÉ DES SCIENCES
DE L'ACADÉMIE DE PARIS, ETC., ETC., ETC.

DEDICATION PAGE OF THENARD'S "*Traité de Chimie*," A FIVE-VOLUME WORK

the French chemist, P. Lebeau (*27*), (*29*). After adding potassium or sodium fluoride to pure beryllium fluoride to make it conduct the current, he placed the mixture in a nickel crucible. After melting the double salt with a Bunsen burner, he placed the positive (graphite) electrode in the fluoride mixture and connected the nickel crucible to the negative side of a battery of twenty amperes under eighty volts. In less than an hour crystals of beryllium were deposited on the sides of the crucible. After washing them, first with water and then with absolute alcohol, and drying them in a vacuum desiccator containing phosphorus pentoxide, Lebeau found that they contained from 99.5 to 99.8 per cent of beryllium. This research provided the data for his thesis for the doctorate in June, 1898.

Nearly a century after Wöhler and Bussy liberated beryllium, Alfred Stock and Hans Goldschmidt devised the first commercial process, in which a mixture of the fluorides of beryllium and barium is electrolyzed. The molten beryllium separates out at the water-cooled iron cathode (*24*).

Boron

There is no conclusive proof that the ancients were acquainted with borax; even in the eighteenth century, it was believed to be an artificial production (*59*), (*60*). In 1772, however, the Swedish merchant Johan Abraham Grill (Abrahamsson) described in volume thirty-four of *Vetenskapsacademiens Handlingar* a natural borax called *pounxa* sent him from Thibet by Jos. Vit. Kuo, a native Chinese Catholic missionary. "From the report of my correspondent Vit. Kuo," said he, "it can be in-

LOUIS-JOSEPH GAY-LUSSAC
1778–1850

Professor of chemistry at the École Polytechnique and at the Jardin des Plantes. With Thenard, he prepared potassium without the use of a battery, and isolated boron. In 1809 Gay-Lussac enunciated his famous law of combining volumes of gases.

ferred that the *pounxa* is found in Thibet, that to obtain it one digs into the ground to the depth of two yards;. . .it positively cannot be made artificially by heating the earth; it is found already prepared by nature" (*61*).

Analyses by R. Nasini and R. Grassini indicate that boric acid entered into the composition of the brilliant coral red glazes on the Aretine vases (first century B.C. to first century A.D.) excavated at Arezzo (*57*), (*76*). Because of the seal, or impression, on the bottom, these vases were known as "terra sigillata ware." Paul Diergart of the research staff of the Royal Porcelain Works in Berlin questioned these analyses, however (*58*).

Boric acid was first prepared in 1702 by Wilhelm Homberg. He was born on January 8, 1652, at Batavia on the island of Java. When his father left the service of the Dutch East India Company, the family settled in Amsterdam, where young Wilhelm (or Willem) had a much better opportunity to study than in the torrid climate of the East Indies. After studying law at Jena and Leipzig, he was admitted to the bar in Magdeburg in 1674. Soon becoming more interested in the laws of nature than in those devised by man, he began to devote much time to botany, astronomy, and mechanics.

The Burgomaster of the city, Otto von Guericke, was then performing "the Magdeburg miracles" with the evacuated hemispheres which sixteen horses could not separate and with his curious barometer, "the little man who remained hidden in a tube when the weather was to be rainy and came out when it was to be fair" (*62*). These wonders still further diverted Homberg's attention from his practice of law.

At Padua and Rome, he studied medicine, optics, art, and music. After further study in France, he went to England to work with Robert Boyle, thence to the Netherlands, where he studied anatomy, and finally to Württemberg, where he received the degree of doctor of medicine. Homberg then visited the mines of Saxony, Hungary, and Bohemia, and went to Sweden to see the great copper mine at Fahlun and work with Urban Hiärne in the newly established chemical laboratory at Stockholm. When Homberg returned to Paris, the Duke of Orleans studied under him, caught his enthusiasm, and equipped for him "the most superb and best furnished laboratory Chemistry had ever seen" (*62*).

In 1702 Homberg stated in the Memoirs of the Academy of Sciences at Paris that he had heated borax with a solution of iron vitriol (ferrous sulfate) and sublimed off with the water vapor a substance which he called *sel volatil narcotique du vitriol* ("volatile sedative salt from the vitrol"). Thus it is evident that he must have prepared boric acid and that he believed that it came from the ferrous sulfate (*63*). He used hot water to extract the colcothar or residue which remained in the retort after distillation of Nordhausen sulfuric acid, filtered the solution, and mixed with it a hot solution of borax. After evaporating the mixture to incipient crystallization, he heated it on a sandbath, using a cucurbit and alembic. When the liquid products of distillation ceased to drip into the receiver, snow-white platelets with a mother-of-pearl luster sublimed in the still-head. By redistilling the aqueous distillate eight or ten times, Homberg obtained a good yield of the "sedative salt" (*63*).

F. M. Jaeger found in the correspondence of Elisabeth Charlotte of Orleans (1652–1721) a firsthand character sketch of the discoverer of boric acid. "One cannot know Homberg," said she, "without admiring him for his clear mind,—not at all confused as the highly educated usually are, and not solemn, but always jolly; everything he knows, even the most difficult arts, seem with him to be a jest, as though he were playing tricks. . . . He has a soft voice, and speaks very slowly but clearly" (*64*).

During his last illness, Homberg's patience "was that of a hero or a saint. A few days before his death," said Fontenelle in his eulogy, "he took the liberty of writing to His Royal Highness the Duke of Orleans. . . to recommend to him all that he had most loved, the widow whom he was about to leave and the Academy of Sciences. His prayer for the Academy had more success than he would have dared to hope; the prince has reserved for himself alone the direct management of this Company. He treats our sciences like his own domain, of which he is jealous" (*62*).

Wilhelm Homberg died on the twenty-fourth of September, 1715. "Although he had a weak constitution, he was most industrious; although he lacked strength, he had courage to compensate for it. Besides a prodigious quantity of curious facts of natural philosophy collected in his mind and retained in his memory, he had the qualifications of an ordinary scholar in history and languages. He even knew Hebrew. His quality of mind is evident in all his work: above all, an ingenious attentiveness which caused him to make observations where others saw nothing. . . .

"We have already mentioned his complete freedom from ostentation," said Fontenelle. "He was equally free from mystery, so common among chemists, which is merely another kind of ostentation in which one conceals instead of displaying. . . . Although French was always a foreign language for him and he naturally was not rich in vocabulary and had continually to search for the right word, he always found it. No one ever had more gentle manners nor more sociable habits. . . . A wholesome, peaceful philosophy made him receive calmly the different events of life, immune to those agitations for which one has, if one wishes, so many occasions" (*62*).

In 1747–8 Théodore Baron de Hénouville (1715–1768) proved that borax is composed of "sedative salt" and soda (*65*). In his "Elective Attractions," Torbern Bergman stated emphatically that the so-called "sedative salt" is not a salt but an acid. "The substance commonly called sedative salt," said he, "is more nearly allied to acids than any other class of bodies. It reddens turnsole and saturates alkalis and soluble earths. It also dissolves various metals, and has other properties which shew its acid nature; and it seems better entitled to the name of acid of borax than to that of sedative salt" (*66*).

After the chemical revolution, "sedative salt" came to be regarded as an acidic oxide, boric (or boracic) acid. Even at the close of the eighteenth century, its chemical nature was not understood. In a letter to the *Annales de Chimie et de Physique,* A. N. Scherer wrote in 1799: "I have just been assured that Crell has recognized carbon as the radical of boracic acid" (*67*).

Lavoisier believed that it contained oxygen, and had mentioned its radical in his list of elements* (*20*). The first proof of the composition of boric acid was given in 1808 when Gay-Lussac and Thenard in France and Davy in England succeeded in decomposing it by reduction with potassium, and in liberating a new element which the French chemists called *bore* and Sir Humphry called *boracium.*

Louis-Joseph Gay-Lussac was born at St. Léonard, near Limoges, on December 6, 1778, and was therefore just eleven days older than Davy. After receiving his elementary education in St. Léonard he went to Paris, and when he was nineteen years old, he enrolled at the École Polytechnique, where he soon became acquainted with his lifelong friend and collaborator, Thenard.

LOUIS-JACQUES THENARD
1777–1857

Professor of chemistry at the École Polytechnique. Discoverer of hydrogen peroxide. Collaborator with Gay-Lussac in his researches on potassium, boron, iodine, and chlorine. He also investigated many fatty acids, esters, and ethers.

Somewhat later he won the friendship of Berthollet at the École des Ponts et Chaussées, who said to him, "Young man, your destiny is to make discoveries" (*3*). For a time he worked with Berthollet's son in a factory in Arcueil where chlorine was used to bleach linen. On New Year's day in the year 1802 Gay-Lussac became a répétiteur at the École Polytechnique, where he often substituted for Fourcroy in his lectures on chemistry.

Two years later Gay-Lussac and Biot made a daring balloon ascension to study the behavior of a magnetic needle and the chemical composition of the atmosphere at high altitudes.

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* See Part XV, pp. 272.

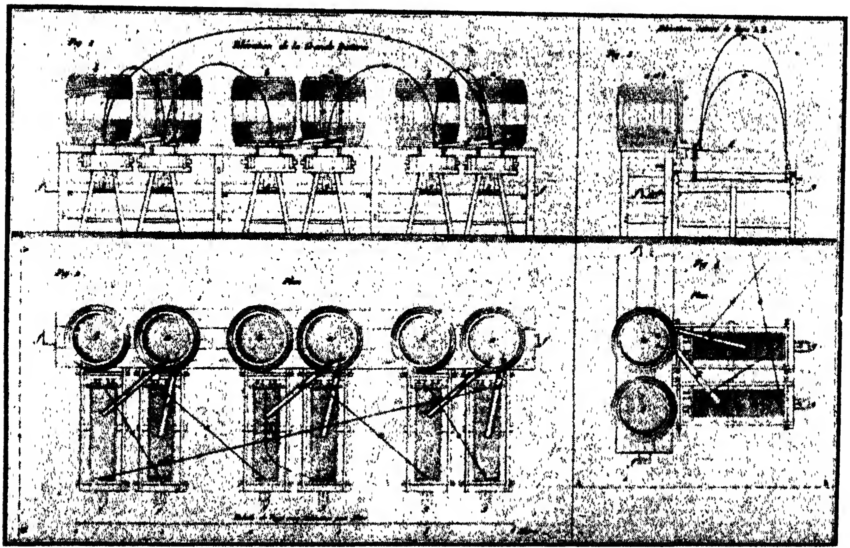
On another occasion, when Gay-Lussac alone had reached an elevation of 7016 meters and wished to ascend still higher, he threw overboard some small objects to lighten the balloon. A shepherdess in the field was astonished to see a white wooden chair fall from the sky into some bushes, and the peasants who heard her story were at a loss to explain why, if the chair had come direct from Heaven, the workmanship on it should be so crude (*3*).

From Appleton's "Beginners' Hand-Book of Chemistry"

GAY-LUSSAC AND BIOT MAKING THEIR BALLOON ASCENSION

Gay-Lussac was then twenty-five years old.

After a period of extended travel and study in Italy with von Humboldt, Gay-Lussac returned to the École Polytechnique and began a long series of researches with Thenard. Louis-Jacques Thenard,* a carpenter's son, was born at La Louptière near Nogent-sur-Seine on May 4, 1777. After receiving private instruction from the village priest, he went to Paris to study chemistry, where, after three years of hard study and severe privations, he finally succeeded in winning the recognition of Vauquelin and Fourcroy. The latter scientist had befriended the poor peasant boy Vauquelin in his early struggles, and now Vauquelin in turn helped Thenard to obtain a teaching position in a Parisian pension. In 1798 Gay-Lussac and Thenard met at the École Polytechnique, where both later became professors.



From Gay-Lussac and Thenard's "Recherches Physico-Chymiques"

THE GREAT BATTERY THAT NAPOLEON PRESENTED TO THE ÉCOLE POLYTECHNIQUE

The scale is 25 mm. for 1 meter. Figs. 1 and 2. Elevation and plan of the great battery. Figs. 3 and 4. Elevation and plan of two cells. *a,a,a.* Barrels containing liquid for filling the troughs. *b,b,b.* Barrels containing water for washing the troughs. *c,c,c.* Lead siphons for the flow of liquid from the barrels. *d,d,d.* Conduits for receiving liquid from the barrels by means of the siphons, and conducting it into the troughs. *e,e,e.* Wires connecting the different cells of the battery. *f,f,f.* Trough for receiving liquid from all the cells by means of the individual troughs, *g,g*.

When the news of Davy's isolation of the alkali metals reached Paris in 1808, Napoleon provided Gay-Lussac and Thenard with a powerful voltaic pile. Before it could be set up, however, they showed that these metals can be obtained without a battery simply by reducing the caustic alkali with metallic iron at a high temperature, a method which Davy

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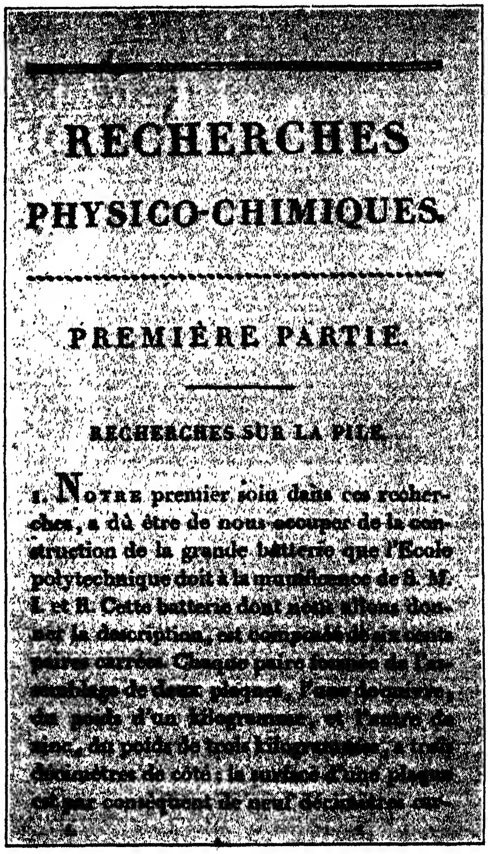
* He always spelled his name thus, without the acute accent over the *e*.

soon adopted in preference to his own. The potassium which the French chemists prepared in this manner was soon put to good use when they attempted to decompose boric acid.

On June 21, 1808, a note from Gay-Lussac and Thenard was read before the Institute. It announced that the results they had obtained by treating boric acid with potassium could be explained only by admitting that that acid is composed of a combustible substance and oxygen (*21*). At the time this notice was read, Gay-Lussac was seriously ill as the result of an explosion in which he had almost lost his sight (*30*).

Before regarding their proof as complete Gay-Lussac and Thenard wished not only to decompose boric acid, but to recompose it. On November 30 of the same year they were able to state in the *Annales de Chimie et de Physique* that "the composition of boracic acid is no longer problematical. In fact," said they, "we decompose and we recompose this acid at will." Their method was as follows:

> To decompose it, place equal parts of metal [potassium] and very pure, vitreous boracic acid in a copper tube to which a tube of bent glass is attached. Place the copper tube in a small furnace, with the end of the glass tube in a flask of mercury. When the apparatus is ready, heat the copper tube gradually until it becomes faintly red; keep it in this condition for several minutes; then, the operation being ended, allow it to cool and take out the material.



RECHERCHES

PHYSICO-CHIMIQUES.

PREMIÈRE PARTIE.

RECHERCHES SUR LA PILE.

1. NOTRE premier soin dans ces recherches, a dû être de nous occuper de la construction de la grande batterie que l'Ecole polytechnique doit à la munificence de S. M. I. et R. Cette batterie dont nous allons don-

ON THE FIRST PAGE OF THEIR "*Recherches Physico-Chimiques*" GAY-LUSSAC AND THENARD THANK NAPOLEON FOR THE LARGE BATTERY THAT HE HAD PRESENTED TO THE ÉCOLE POLYTECHNIQUE.

Gay-Lussac and Thenard then gave a detailed description of the experiment, saying:

> When the temperature is about 150 degrees, the mixture suddenly glows strongly, which appears in a striking manner if a glass tube is used. So much heat is produced that the glass tube melts slightly and sometimes breaks, and the air is almost always driven out of the vessel with force. From the beginning to the end of the experiment, only atmospheric air is released, with a few bubbles of hydrogen gas, which do not amount to the fiftieth part of that given off when the metal combines with water. The metal [potassium] is used up decomposing part of the boracic acid; and these two substances are converted by their mutual reaction into an olive gray material which is a mixture of potassium, potassium borate, and the radical of boracic acid. Extract this mixture in a tube by pouring water into it and heating slowly, and separate the boracic radical by washing with cold or hot water. That which does not dissolve is the radical itself. . .

Raffaello Nasini

1854–1931

Italian chemist who reported the presence of boric acid in the glazes of ancient Aretine vases, and studied the rare gases of the boric acid soffioni, or hot springs, of Tuscany. In his youth he assisted Stanislao Cannizzaro and in later life he collaborated with Giacomo Ciamician.

By burning the new "radical" in oxygen, or, better still, by oxidizing it vigorously with potassium chlorate, potassium nitrate, or nitric acid, Gay-Lussac and Thenard were able to make some synthetic boric acid, a sample of which they presented to the Institute. As a result of their experiments they concluded "that this body, which we now propose to call *bore*, is of a definite nature, and can be placed beside carbon, phosphorus, and sulfur; and we are led to think that to pass into the state of boracic acid it requires a great quantity of oxygen, but that before arriving at that state it first passes through that of the oxide" (*21*), (*38*).

In the following year Gay-Lussac gave an even greater contribution to chemistry, his statement of the famous law of combining volumes. In later life he taught chemistry both at the École Polytechnique and at the Jardin des Plantes. After Courtois discovered iodine in 1811, Gay-Lussac and Thenard made a thorough study of its properties, and published their results in a memoir now treasured by chemists as a great scientific classic. Gay-Lussac died in Paris on May 9, 1850 (*3*). Davy once said of him, "Gay-Lussac was quick, lively, ingenious, and profound, with great activity of mind, and great facility of manipulation. I should place him at the head of all the living chemists of France" (*4*).

Besides carrying out many inorganic researches with Gay-Lussac, Thenard made important contributions to organic chemistry. He outlived his famous collaborator by seven years, and when he died on June 21, 1857, at the age of eighty years, his native village honored him by changing its name to La Louptière-Thenard (*3*).

Davy's method of isolating boron was very similar to that of the French chemists. While engrossed in the study of the alkalies, he had passed a current through boric acid and had noticed a dark, combustible substance at the negative pole, but had not at that time thoroughly investigated it (*36*). In the following year, however, he placed a mixture of boric acid and potassium in a copper tube and heated it to dull redness for fifteen minutes. When he examined the contents, he found that the potassium had disappeared and that in its place there was an olive-gray powder which did not effervesce when treated with water or with acids. Davy's paper announcing the discovery of metallic boron was read before the Royal Society on June 30, 1808 (*28*), (*30*).

In 1909, Dr. E. Weintraub of the General Electric Company ran high-potential alternating current arcs between cooled copper electrodes in a mixture of boron chloride with a large excess of hydrogen (*51*), obtaining pure fused boron which differed greatly in properties from the impure amorphous product of earlier workers.

Silicon

Although Sir Humphry Davy felt certain that silica is not an element, he was unable to decompose it with his powerful voltaic pile, and was also unsuccessful in his attempts to isolate silicon by passing potassium vapor over red-hot silica. Gay-Lussac and Thenard observed that silicon tetrafluoride and potassium react violently when the metal is heated, and that a reddish brown, combustible solid is obtained. This was probably very impure amorphous silicon (*37*), (*39*).

Berzelius heated a mixture of silica, iron, and carbon to a very high temperature, and obtained iron silicide. When he decomposed this with hydrochloric acid, silica was precipitated, and the amount of hydrogen evolved was in excess of the iron, indicating that some other metal must be present (*9*).

Berzelius finally showed in 1824 that this other seemingly metallic substance was derived from the silica, and succeeded in preparing the amorphous form of it by two methods. In the first of these he heated potassium in an atmosphere of silicon tetrafluoride gas, as Gay-Lussac and Thenard had done, and obtained a brown mass. When this was thrown into water, hydrogen was freely evolved, and the new element silicon was precipitated as a dark brown, insoluble powder containing potassium fluosilicate, which is difficultly soluble. Although Davy, Thenard, and Gay-Lussac had all handled the brown powder before, only Berzelius had the patience for the prolonged washing required to remove the fluosilicate (*9*), (*32*).

In his other method Berzelius heated the potassium fluosilicate with excess potassium. The resulting potassium silicide was easily decomposed with water, the amorphous silicon settling to the bottom.

> Nothing is easier [said he] than to procure this substance; the following is the method I have adopted: The double fluate of silica and potash, or soda, heated nearly to redness to drive off the hygrometric water, is put into a glass tube, closed at one end. Bits of potassium are added and mixed with the powder by fusing the metal and gently rapping the tube. It is then heated by the spirit-lamp, and before it is red-hot, a feeble detonation ensues and the silicium is reduced. The mass is suffered to cool, and then treated with water as long as it dissolves anything. Hydrogen gas is at first evolved, in consequence of siliciuret of potassium having been formed, which cannot exist in water.
>
> The washed substance [continued Berzelius] is a hydruret of silicium, which, at a red heat, burns vividly in oxygen gas, although the silicium is not thereby completely oxidated; it is then heated in a covered platina crucible, the heat being slowly raised to redness. The hydrogen alone is oxidated, and the silicium is now no longer combustible in oxygen, but chlorine attacks it readily. The small portion of silica that is formed may be dissolved by fluoric [hydrofluoric] acid. If silicium has not been exposed to a strong red heat, the acid dissolves it, with a slow disengagement of hydrogen. According to my synthetical experiments, silica contains 0.52 of its weight of oxygen.

Berzelius' product was impure amorphous silicon. Zirconium may be obtained by an analogous process (*32*).

The first crystalline silicon was prepared by Henri Sainte-Claire Deville in 1854 (*9*), (*31*). In the course of his researches on aluminum, he decomposed an impure sodium aluminum chloride with the voltaic pile, and obtained a gray, brittle, granular melt containing 10.3 per cent silicon. When he dissolved away the aluminum, some shining platelets remained.

Sainte-Claire Deville explained his results by saying that an alloy often behaves like a true solution of one metal in another. "Thus it is," said he, "that carbon, boron, and silicon, dissolving like metals in iron and in aluminum, separate from them in cooling, and can be obtained in the crystalline state by the use of reagents which act on the aluminum and the iron without attacking the carbon, the boron, and the silicon. This is the principle of the method which has served for the preparation of the last two metalloids in the adamantine state." In spite of the metallic luster of his crystalline silicon, he realized that the element was not a true metal. "On the contrary," said he, "I think this new form of silicon bears the same relation to ordinary silicon that graphite does to carbon" (*33*), (*34*), (*35*).

Aluminum

Aluminum is the most abundant metal on the earth's surface and one of the most useful ones, yet it remained unknown for many centuries. Early alum works in Phocis near Ionia and in Lesbos sold their product to the Turks for the manufacture of brilliant Turkey red (*68*), (*69*). The manufacture was also carried on in Syria, at Foya Nova near Smyrna, and at Constantinople. In 1254 A.D., Friar William De Rubruquis (Ruysbroek) wrote in his journal, "I found many Frankes at Iconium [Konia], and a certaine Januensian Marchant, called Nicholas de Sancto Syrio. Who with a certaine companion of his a Venetian, called Boniface de Molendino, carried all the Allum out of Turkie, so that the Soldan could not sell any, but to those two: and they made it so deare, that what was wont to be sold for fifteene Bizantians, is now sold for fifty" (*70*).

In about 1459 Bartholomew Perdix (Bartolomeo Perdice, or Pernice), a Genoese merchant who had been in Syria, found a rock suitable for alum on the island of Ischia; he has been regarded as the first to introduce this industry into Europe (*68*). Gino Testi gives evidence, however, that alum was manufactured in Italy long before this. He quotes a passage from Diodorus Siculus (first century B.C.) which shows that the Romans profitably exported alum from Lipari for use in Phoenician dyeing. According to Testi, the alum mines on the island of Ischia have been known since the twelfth century A.D., and Perdice, already aware of their richness, brought skilled workmen from Genoa who had learned the trade in Rocca (Orfa) but had fled from Asia because of the Turkish conquests (*71*).

Before 1454 Giovanni de Castro learned the process at Constantinople. On returning to Italy after that city had fallen into the hands of the Turks he happened to find, in about 1462, in the barren hills near Tolfa, some holly plants like those he had seen growing near the alum mines in Syria. On searching, he found some white stones similar to the Syrian ore from which alum was prepared (*71*). Unemployed alum-workers, brought from Genoa, "thanked God for having restored to them their means of subsistence." For this discovery Pius II granted Giovanni de Castro a generous annuity and had a statue erected in his honor (*71*). In the alum works at Tolfa, Genoese workmen dissolved the calcined rock in a large volume of water, boiled the lye in leaden caldrons, and allowed it to evaporate spontaneously in wooden vats (*69*), (*72*). The so-called "Roman alum" produced there was the double basic potassium alum, which crystallizes in cubes rather than octahedra (*71*), (*73*).

Although G. E. Stahl and Caspar Neumann both believed that alum contained lime, J. H. Pott was unable to prepare it from lime and vitriolic acid, but always obtained merely selenite (calcium sulfate) (*74*). When Stahl leached with water a broken clay tube he had used for distilling spirit of vitriol (sulfuric acid), he obtained crystals of alum (*74*). Pott, too, prepared alum from clay and sulfuric acid (*74*).

In an attempt to determine the composition of alum, A. S. Marggraf in 1754 added pure alkali to several pounds of it and precipitated what he called the "earth of alum" (Alaunerde). After he had thoroughly washed and dried this alumina, he tried in vain to regenerate the alum by adding sulfuric acid.

Marggraf then collected clays from various places in Germany, Silesia, and Poland, and distilled them with sulfuric acid, but obtained no satisfactory crystals of alum. When he added fixed alkali in the proper amount, however, he obtained beautiful, large crystals of it (*74*).

Marggraf noticed that, when he dissolved the earth from alum in nitric acid, evaporated the solution, and calcined the residue, he merely regenerated the "earth" but obtained no "Balduin's phosphorus" (calcium nitrate). He realized, therefore, that the earth in alum must be different from that in chalk or limestone. He also demonstrated the presence of alumina in clay and in roofing slate (*74*).

Marggraf was born in Berlin on March 3, 1709, studied chemistry and pharmacy first under his father and then under Caspar Neumann, took the medical course at Halle, and received further chemical and metallurgical training in Freiberg from the famous director of mines, J. Fr Henckel. He devoted fifty years of his life to scientific research, and was a pioneer in analytical chemistry. He proved that potash and soda are different, that calamine contains a peculiar metal, zinc, and that alumina, magnesia, and lime are three distinct earths, and was one of the first persons to prepare phosphorus. Marggraf died in his native city on August 7, 1782, at the age of seventy-three years. D. Lorenz Crell called him the second father of European analytical chemistry (*10*), and he must also have been a great teacher. One of his most famous pupils was Franz Karl Achard (*40*).

Condorcet once said of Marggraf, "Perhaps no physicist ever so completely excluded every system and hypothesis. . .if, for example, he admits Stahl's doctrine on phlogiston, one would think, from the reserve with which he speaks of it, that he had a presentiment that this doctrine, then so widely accepted, would soon, at least, be overthrown. His memoirs confine themselves to the statement of the facts. . .his results have a precision which was not known before him. . ." (*75*).

In his eulogy, Condorcet said that "M. Marggraf had a kind, good-natured, happy temperament; his only distraction and his greatest pleasure except study was a small circle of friends and enlightened men who could understand him and to whom he could say what he believed" (*75*).

The attempts of Berzelius and Davy to use the voltaic current for isolating the metal present in alumina were unsuccessful. Although most chemical historians credit Wöhler with the first isolation of aluminum, the claims of Oersted cannot be lightly dismissed (*11*), (*42*).

Hans Christian Oersted (*41*) was born on Langeland Island in southern Denmark in 1777, the year in which Lavoisier overthrew the phlogiston theory. His father was a rather unsuccessful apothecary, who had very little money for the education of his children. Hans Christian learned arithmetic alone out of an old schoolbook and sometimes received a little instruction from private tutors. When he was twelve years old he became his father's assistant in the pharmacy, where he soon learned to enjoy his chemical duties. As he was very eager to attend the University of Copenhagen, he studied conscientiously until, at the age of seventeen years, he had earned the coveted certificate (*Reifezeugnis*) entitling him to matriculation. His studies at Copenhagen included science, philosophy, and medicine, and at the age of twenty-two years he received the degree of Doctor of Medicine.

From Oersted's "The Soul in Nature"

HANS CHRISTIAN OERSTED
1777-1851

Danish physicist, chemist, physician, and pharmacist. Discoverer of the magnetic action of the electric current. The first person to isolate the metal aluminum.

At this time he began to lecture on chemistry and metaphysics, and took over the management of a pharmacy. After Volta's discovery became known, Oersted immediately became interested in physics and electricity. When he visited the famous universities in Germany, the scientists he met were charmed by his active mind, his youthful enthusiasm, and his almost childlike appearance and bearing. In 1806 he became a professor of physics at the University of Copenhagen. His fame rests chiefly on his epoch-making discovery of the magnetic action of the electric current and the close relation between electricity and magnetism.

In 1825, however, he studied the chemical action of the voltaic current, and tried to isolate chemically the metal believed to be present in alumina. He first prepared liquid aluminum chloride by passing a current of chlorine gas over a mixture of charcoal and alumina heated to redness. By allowing potassium amalgam to react with the aluminum chloride, he prepared an aluminum amalgam, and by distilling off the mercury out of contact with the air, he obtained a metal that looked like tin (*11*).

Oersted gave the following description of his method:

> The compound of chlorine with the combustible element of the clay (aluminum chloride) is volatile at a temperature which is not much above that of boiling water; it is somewhat yellowish, perhaps however from admixed carbon; it is soft, but still has crystalline form; it absorbs water with avidity and dissolves therein with great ease and with evolution of heat. Rapidly heated with potassium amalgam, it is decomposed, potassium chloride and aluminum amalgam being formed. This amalgam is very quickly decomposed in contact with the atmosphere. By distillation without contact with the atmosphere, it forms a lump of metal which in color and luster somewhat resembles tin. Moreover the author has found, both in the amalgam and the aluminum, remarkable properties which do not permit him to regard the experiments as complete, but show promising prospects of important results (*42*), (*43*).

Oersted's product must have been impure, metallic aluminum containing mercury, but when Wöhler repeated the experiment he found that the gray molten mass formed by the action of the potassium amalgam on the aluminum chloride volatilized completely when heated (*12*), (*46*). Kirstine Meyer's careful study of Oersted's unpublished notes and I. Fogh's and Tosterud and Edwards' repetitions of his experiment show that the great Danish physicist allowed a dilute amalgam containing about 1.5 per cent of potassium to react with excess aluminum chloride, and that it is possible to prepare the metal in this manner (*42*), (*44*), (*45*), (*53*).

Since Oersted's results were published in an obscure Danish journal, they made little impression on the scientific world. Nevertheless, his discovery of electromagnetism brought him the prizes, honors, and influence he so richly deserved. He lived to be seventy-four years old (*41*).

Friedrich Wöhler, one of the most versatile chemists Germany ever produced, was born in the little village of Eschersheim near Frankfort-on-the-Main on July 31, 1800. His father, who himself had a keen appreciation of Nature and a liking for experimentation, delighted to see the same tastes and talents develop in the young child. At the age of fourteen years Wöhler entered the gymnasium at Frankfort, where he was regarded as an average student. As he was passionately absorbed in collecting minerals and making chemical experiments, he frequently neglected his assigned lessons, but these hobbies led him to make the acquaintance of some famous mineral collectors, among them Johann Wolfgang von Goethe (*13*).

From Muspratt's "Chemistry, Theoretical, Practical, and Analytical"

FRIEDRICH WÖHLER
1800–1882

German chemist. Student of Leopold Gmelin and Berzelius He was the first person to synthesize urea and to describe the properties of metallic aluminum. He isolated aluminum, beryllium, and yttrium by the action of potassium on the respective chlorides.

Wöhler was always greatly interested in new elements. Soon after Berzelius discovered selenium in Swedish sulfuric acid, Wöhler found that the Bohemian acid also contained it. Soon after Professor Stromeyer discovered cadmium, young Wöhler sent him some that he had prepared from zinc. Wöhler's great ambition was to make potassium, but since his voltaic pile made of alternate layers of Russian copper coins and zinc plates was not powerful enough for this, he devised a purely chemical method, somewhat similar to that of Gay-Lussac and Thenard, in which he heated a mixture of potash and charcoal to white heat in a graphite crucible. Since his sister shared the exhausting labor of blowing the bellows, she rejoiced as much as he did when the shining globules of metallic potassium appeared (*13*).

The youthful Wöhler also had many other interests. He won prizes in mathematics, made oil paintings and etchings, collected coins and other small objects from Roman ruins, and read with enjoyment the best German poetry. At the age of nineteen years he began his medical course at the University of Marburg, but in the following year he transferred to Heidelberg in order to study under Leopold Gmelin (*47*). He was deeply interested in medicine, and intended to become a practicing physician specializing in obstetrics. On September 2, 1823, he received the degree of Doctor of Medicine, Surgery, and Obstetrics, *insigni cum laude* (*13*).

He had continued his chemical experiments all through his medical course, and Professor Gmelin, who had not failed to notice his surprising skill, advised him to relinquish medicine for chemistry. Wöhler therefore wrote to Berzelius for permission to enter his laboratory in Stockholm. On August 1 the great Swedish master gave his famous reply: "One who has studied under the direction of Herr Leopold Gmelin will certainly find little to learn with me......You may come when you wish."

Berzelius must have realized at once that he had a remarkable student, for he started out by assigning him the difficult analysis of a zeolite. If Berzelius had a remarkable student, however, Wöhler also had a most unusual teacher, for he first went through the entire analysis himself, showing his student the details of every operation. Whenever Wöhler worked too hastily, Berzelius remarked, "Doctor, that was quick, but poor"* (*13*). Although Wöhler spent less than a year in Stockholm, the teaching of Berzelius influenced the whole course of his life and, like his great master, he made important contributions both to organic and to inorganic chemistry. Minds such as these cannot be encompassed within narrow boundaries. As long as Berzelius lived, he carried on a lively correspondence with Wöhler, and these letters are a rich source of pleasure and profit to all chemists interested in the history of their science.

From Muspratt's "Chemistry, Theoretical, Practical, and Analytical"

LEOPOLD GMELIN
1788–1853

Professor of chemistry and medicine at Heidelberg. First author of the "*Handbuch der anorganischen Chemie.*" Discoverer of potassium ferricyanide. Son of Johann Friedrich Gmelin, the author of the "*Geschichte der Chemie.*" Leopold's nephew, Christian Gottlob Gmelin, was the first to observe the red color imparted to a flame by lithium salts.

In 1825 Wöhler became a member of the chemistry faculty at the University of Berlin, and in 1828 he was made a full professor. It was here that he made the two great discoveries for which his name will always be honored: the isolation of aluminum and the synthesis of urea.

THIS WÖHLER PLAQUE, CAST IN ALUMINUM, WAS PRESENTED TO DR. F. B. DAINS BY DR. HOWARD M. ELSEY, WESTINGHOUSE RESEARCH LABORATORY, EAST PITTSBURGH, PENNSYLVANIA.

For the history of it, see ref. (*50*).

As previously stated, Wöhler was unable to obtain metallic aluminum by Oersted's method. However, since the latter encouraged him to continue his attempts, he prepared some anhydrous aluminum chloride by Oersted's method, and devised a new plan for isolating the metal. After adding an excess of hot potassium carbonate solution to a boiling hot solution of

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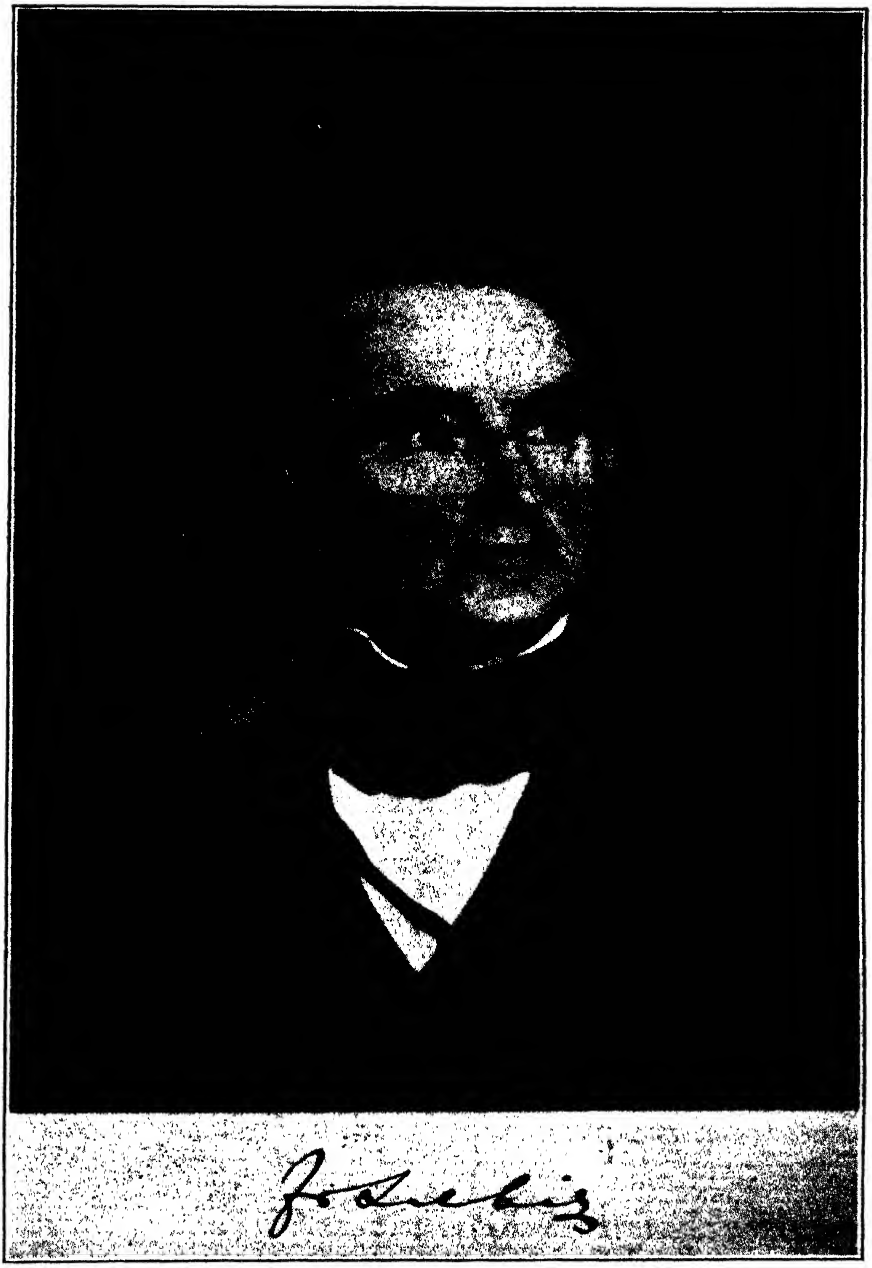
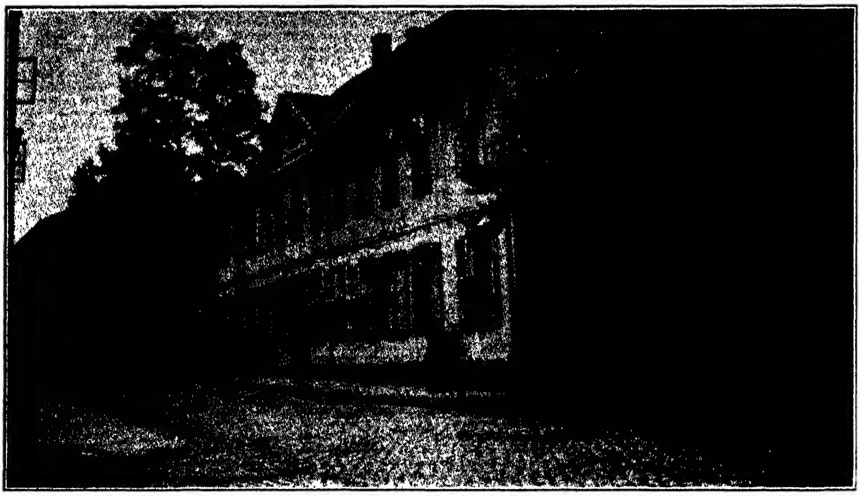
* *"Doctor, das war schnell, aber schlecht."*



Justus von Liebig
1803–1873

German organic and agricultural chemist. Professor of chemistry at Giessen. Friend and collaborator of Wöhler. Discoverer of the isomerism of silver fulminate and silver cyanate. Editor of the *Annalen*. He devised a new combustion train for determining the ultimate constituents of organic compounds, and proved that animal heat and energy are produced by the combustion of food in the body.



WÖHLER'S RESIDENCE AT GÖTTINGEN

alum, he washed and dried the precipitated aluminum hydroxide, and mixed it with powdered charcoal, sugar, and oil to form a thick paste. Upon heating this paste in a closed crucible, he secured a very intimate mixture of alumina and charcoal, and upon passing a current of dry chlorine gas over this red-hot black mixture, he obtained anhydrous aluminum chloride (*12*), (*46*).

Wöhler once said that the method by which he isolated aluminum in 1827 was based on the decomposition of anhydrous aluminum chloride by potassium and on the stability of aluminum in presence of water. Since the reaction is too violent to be carried out in glass, he used a platinum crucible with the cover wired on. Although only gentle heat was applied to start the reaction, the crucible soon became white hot. It was not badly attacked, but in order to prepare aluminum free from platinum he repeated the experiment, using porcelain and Hessian crucibles. When he cooled the crucible completely and plunged it into water, metallic aluminum always separated as a gray powder. Wöhler obtained only a small quantity of the metal, and it was not pure, but contaminated with potassium, platinum, or aluminum chloride (*12*). However, he was the first to describe the properties of aluminum, and in 1845 he finally succeeded in melting the powder to a coherent metallic mass (*49*), (*54*). He also prepared beryllium and yttrium in the same manner (*8*).

Wöhler's life was a long and eventful one. In spite of his unceasing labors for science, he found time for many social contacts, and had a deep capacity for friendship. The lifelong intimacy between Wöhler and Liebig caused the latter to write in one of his last letters:

> Even after we are dead and our bodies long returned to dust, the ties which united us in life will keep our memory green, as an instance—not very frequent—of two men who wrought and strove in the same field without envy or ill feeling, and who continued in the closest friendship throughout (*14*).

In 1835 Wöhler became Stromeyer's successor as professor of chemistry at Göttingen, where he taught for the rest of his life. Wöhler spent his old age in the midst of his happy family. He had a son and four daughters, and when they all visited their parents in the summer, some of them stayed with the neighbors, for the family home was not large enough to hold all the grandchildren. He received high scientific honors of all kinds, but none were dearer to him than the celebrations planned by his students on the occasions of his sixtieth, seventieth, and eightieth birthdays, and on the fiftieth anniversary of the synthesis of urea (*13*), (*48*).

The late Dr. Edgar Fahs Smith, America's great chemical historian, once gave the following picture of the aged Wöhler:

> Two or three days before Christmas the chemical laboratories in the University of Göttingen were nearly deserted. Only a few students remained. Late in the afternoon, some one began singing, "Stille Nacht, Heilige Nacht." One by one the other students in the laboratory gathered about the singer and solemnly joined in the song. Soon we noticed that the door of the laboratory opened and in walked the old Master. Immediately he took from his head the black skull cap he was accustomed to wear in the laboratories, placed it under his arm, folded his hands, and with bowed head stood just inside the door while the song continued. When the singing was over the old Master came forward and said, "Thank you, gentlemen," and withdrew (*15*).

LOUIS-LÉONCE ÉLIE DE BEAUMONT
1798–1874

French geologist and mining engineer. Perpetual secretary of the Académie des Sciences. He described the course of great rivers and the effects of their mechanical work, and investigated the materials ejected by volcanoes. With Dufrénoy he made the first accurate and complete geological map of France.

Wöhler's room was filled with portraits of his two best friends, Liebig and Berzelius. Not long before his death, he hesitatingly held out to a friend at parting a little box wrapped in paper, saying to him, "Keep it in re-

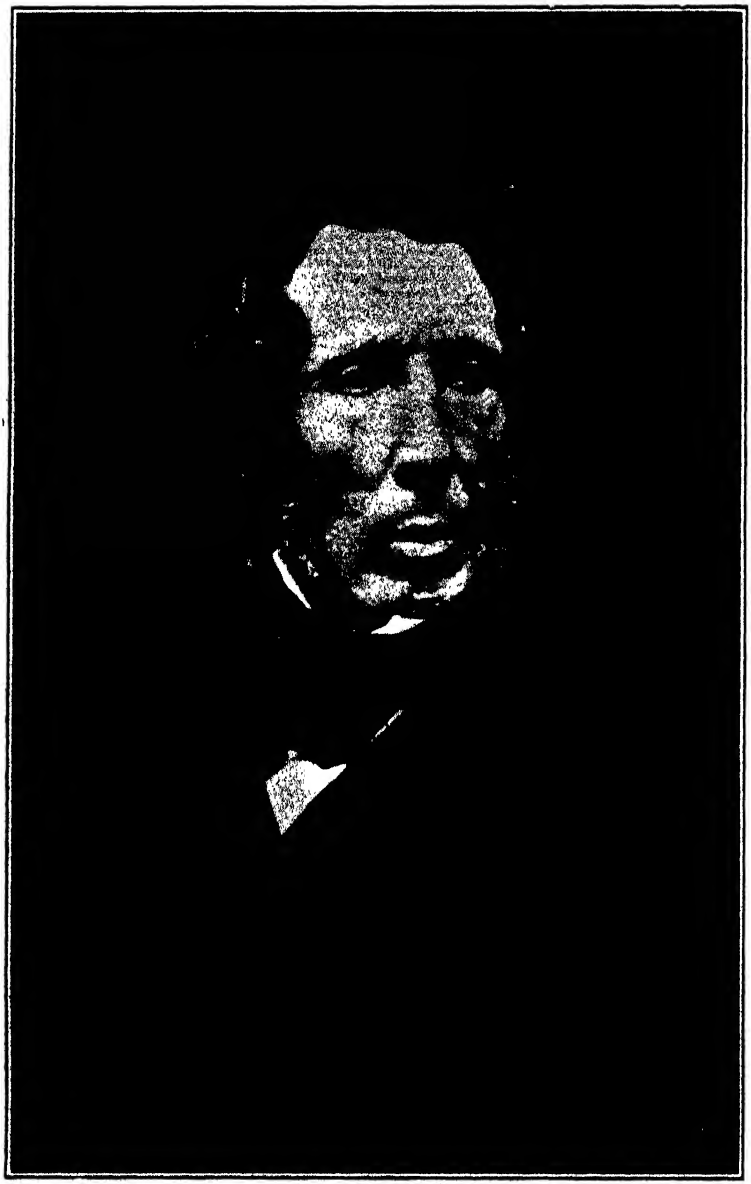


Photo loaned by Frau Hückel, Göttingen, Germany

WÖHLER IN LATER LIFE*

Professor of chemistry at Göttingen. Famous for his researches on cyanogen, cyanuric acid, and the radical of benzoic acid, and on the metals titanium, aluminum, yttrium, beryllium, and vanadium. German translator of Berzelius' "Textbook of Chemistry" and von Hisinger's "Mineral Geography."

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* The author acknowledges her gratitude to the late Dr. L. C. Newell for the use of this portrait.

membrance of me. Do not open it until you are on the train." The box was found to contain a spoon and the words, "A present from Berzelius; he used this platinum spoon many years in his researches." Wöhler died on October 9, 1882. In accordance with his wish, there is no bronze or marble monument to mark his resting place, but only a stone with the name Friedrich Wöhler (*13*).

The first pure aluminum was prepared by the great French chemist, Henri Sainte-Claire Deville, who was born on the Island of St. Thomas in the Antilles on March 11, 1818. Both Henri and his elder brother Charles were educated at the Institution Sainte-Barbe in Paris, where Charles studied geology under Élie de Beaumont at the School of Mines, while Henri took the medical course and studied chemistry under Thenard. Both brothers were crowned by the Institute, and both were in the same section. Throughout their lives they had the deepest affection for one another, and when one of Henri's sons married Charles' daughter, one of the fathers remarked, "My brother and I do not know how to tell which of the two belongs to each of us, whether it is my son who has married his daughter, or my daughter who has married his son" (*16*).

From Gay's "Henri Sainte-Claire Deville, sa Vie et ses Travaux"

CHARLES SAINTE-CLAIRE DEVILLE
1814–1876

French geologist who explored the Antilles, the Azores, and the Canary Islands and studied the allotropic forms of sulfur.

HENRI SAINTE-CLAIRE DEVILLE
1818–1881

Professor of chemistry and dean at the University of Besançon, afterward professor of chemistry at the École Normale Supérieure. He discovered toluene in balsam of Tolu, prepared anhydrous nitrogen pentoxide, and made sodium and aluminum on a commercial scale.

Henri's first paper, published in 1839, was a research on turpentine, and two years later he discovered toluene in balsam of Tolu. His most important work, however, was in inorganic and physical chemistry. In 1844 conservative university officials were horrified to learn of the appointment by Thenard of the twenty-six-year-old Henri Sainte-Claire Deville as dean

Courtesy H. N. Holmes

FRANK FANNING JEWETT
1844–1926

Research assistant at Harvard University, under Wolcott Gibbs. Professor of chemistry at the Imperial University of Japan. Professor of chemistry and mineralogy at Oberlin College. His account of Wöhler's researches on aluminum inspired Charles M. Hall to search for a commercial process for preparing the metal.

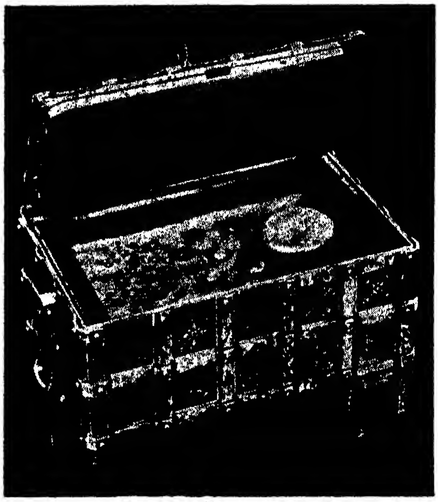
to reorganize the faculty at Besançon. Nevertheless, Thenard's mature judgment proved correct, and Sainte-Claire Deville's career proved to be even more brilliant than he had predicted. While at Besançon, Sainte-Claire Deville devised new analytical methods for testing the city water supply, and succeeded in preparing anhydrous nitrogen pentoxide (*17*).

When Balard, the discoverer of bromine, went to the Collège de France, Deville was called to fill the vacancy at the École Normale Supérieure, and it was there that the first beautiful aluminum ingots were made. Sainte-Claire Deville was attempting in 1854 to prepare a protochloride of aluminum by allowing aluminum to react with the chloride, $AlCl_3$, and in preparing his aluminum he used Wöhler's method, but substituted sodium for the potassium. He noticed some large globules of shining metallic aluminum, and immediately set to work to make the process commercially profitable (*35*).

Although the first experiments were made at the École Normale Supérieure, the generosity of Napoleon III made it possible for him to continue them on a larger scale at the Javel works. Since Sainte-Claire Deville's commercial process required large amounts of sodium, it was necessary for him to perfect at the same time a cheaper process for preparing that metal. When he began his experiments, the price of sodium was even higher than that of potassium, but he knew that sodium compounds are more abundant in Nature than those of potassium, and that sodium, because of its smaller equivalent weight, would be the more economical metal to use.

After perfecting a process for the manufacture of sodium (which caused the price to fall from two thousand francs per kilogram in 1855 to ten francs in 1891), Deville attempted the large-scale production of aluminum. There is found in southern France and elsewhere an ore, bauxite, named for the village of Baux, near Arles in Provence. In the Sainte-Claire Deville process, alumina obtained from this ore is intimately mixed with charcoal and salt, and heated in an atmosphere of chlorine gas, a double chloride of sodium and aluminum being formed, which acts as a flux and allows the aluminum globules to coalesce. The metallic aluminum is then cast into ingots (*18*).

Certain trouble makers who were poor judges of character tried to create ill-will between Wöhler and Sainte-Claire Deville, advising the latter that, since Wöhler's aluminum was of such doubtful purity, he ought to claim for himself the honor of discovering the metal. The French chemist's reaction to this counsel throws an interesting side-light on his character. As soon as he had obtained a sufficient quantity of malleable aluminum, he had a medal cast, bearing simply the name Wöhler and the date 1827, and sent it to the great German master. Deville and Wöhler always remained fast friends, and collaborated in a number of important researches. In his book entitled "L'Aluminium, ses Propriétés, sa Fabrication et ses Applications," the former wrote, "I will say with pleasure that I consider it an unexpected good fortune to have been able to take a few more steps in a path opened by Berzelius' eminent successor in Germany" (*18*).



Courtesy Fisher Scientific Co.

THE ALUMINUM "CROWN JEWELS"

In this chest, carefully preserved by the Aluminum Company of America at Pittsburgh, are the original buttons of the metal made by Charles M. Hall in Oberlin, February 23, 1886 (left), the larger ones made by Hall in December, 1886 (center), and the first button or ingot (right) produced by the Aluminum Company of America.

Henri Sainte-Claire Deville also made important investigations of boron, silicon, magnesium, and the metals of the platinum family. The platinum researches were dangerous, and he often suffered severely from poisoning by the vapors of osmic acid. His fame, however, rests even more on his enunciation of the laws of gaseous dissociation. Sainte-Claire Deville was described as ardent, vivacious, charming, sympathetic, gay, and generous. At the École Normale he used to eat at the students' table, jesting familiarly with them but never for a moment losing their profound respect (*19*). His married life was a most happy one, and his five sons were a credit to their parents. He died in 1881, mourned by his family and by his scientific colleagues throughout the world (*18*), and the funeral oration was delivered by Pasteur.

Courtesy Fisher Scientific Co.

CHARLES MARTIN HALL
1863–1914

American chemist, inventor, metallurgist, and philanthropist who developed a highly successful electrolytic process for manufacturing aluminum. This cheap method of obtaining the metal from its ores made possible the present widespread use of aluminum for domestic, industrial, and transportation purposes.

The next scene of the aluminum drama is laid in the United States. Henri Sainte-Claire Deville's process had made the metal a commercial product, but it was still expensive. Charles Martin Hall, a student at Oberlin College, inspired by the accounts which Professor F. F. Jewett had given of his studies under Wöhler, decided that his supreme aim in life would be to devise a cheap method for making aluminum. In an improvised laboratory in the woodshed, and with home-made batteries, he struggled with this problem. On February 23, 1886, this boy of twenty-one years rushed into his professor's office and held out to him a handful of aluminum buttons. Since these buttons led to a highly successful electrolytic process for manufacturing aluminum, it is small wonder that the Aluminum Company of America now treasures them and refers to them affectionately as the "crown jewels." A beautiful statue of the youthful Charles M. Hall, cast in aluminum, may now be seen at Oberlin College (*11*), (*55*).

Courtesy Hobbs, Bruce Publishing Co.

PAUL-LOUIS-TOUSSAINT HÉROULT*
1863–1914

French metallurgist. Independent discoverer of the electrolytic method of preparing aluminum now known as the Hall-Héroult process. He designed electric furnaces, and made many important contributions to the electrometallurgy of iron and steel.

At about the same time that Hall perfected his process, Dr. Paul-Louis-Toussaint Héroult, a young French chemist of the same age, made the same discovery independently. Dr. Héroult was born in 1863 at Thury-Harcourt in the department of Calvados.† When the war of 1870 broke out, he was sent to live with his grandfather in London, and thus he acquired a good command of the English language. Three years later he returned to France to continue his education.

At the Institution Sainte-Barbe he learned of Sainte-Claire Deville's researches on aluminum, and at the age of fifteen years he read the latter's famous treatise. Using the steam engine and dynamo of a small tannery which he had inherited in 1885, Héroult attempted to electrolyze various

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* The author is most grateful to *Aluminum*, Hobbs, Bruce Publishing Co., for the portrait of Héroult.

† Vauquelin, the discoverer of chromium and beryllium, was also a native of Calvados.

aluminum compounds. In the following year, when he was attempting to electrolyze cryolite, his iron cathode melted. Since the temperature was not high enough to account for this, Héroult realized that an alloy had been formed. A few days later, when he tried to lower the temperature of the electrolytic bath by adding some sodium aluminum chloride, he noticed that the carbon anode was being attacked. He concluded that he must be dealing with an oxide of aluminum, which was being reduced at the expense of the anode. This was indeed the case, for the sodium aluminum chloride he had bought had been previously exposed to moist air and converted into hydrated alumina. The first Héroult patent for this process was announced shortly before the Hall patents (*77*).

M. Héroult also made many important contributions to the electrometallurgy of iron and steel. He made frequent trips to the United States, and when the Perkin Medal was awarded to Charles M. Hall in 1911, M. Héroult crossed the ocean in order to be present at the ceremony and congratulate him. By this gracious act, he proved himself to be a worthy successor of his great, generous countryman, Henri Sainte-Claire Deville (*11*), (*52*). Dr. Héroult and C. M. Hall both died in 1914.

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Courtesy S. E. Sheppard

WILLIAM HENRY FOX TALBOT
1800–1877

English antiquarian, physicist, and pioneer in optics and photography. One of the first to decipher the Assyrian inscriptions at Nineveh. In 1839 he made negative prints on silver chloride paper, and two years later he invented the calotype process for making positives.

XX. SOME SPECTROSCOPIC DISCOVERIES

Many elements are present in the earth's crust in such minute amounts that they could never have been discovered by ordinary methods of mineral analysis. In 1859, however, Kirchhoff and Bunsen invented the spectroscope, an optical instrument consisting of a collimator, or metal tube fitted at one end with a lens, and closed at the other except for a slit at the focus of the lens, to admit light from the incandescent substance to be examined; a turntable containing a prism mounted to receive and separate the parallel rays from the lens; and a telescope to observe the spectrum produced by the prism. With this instrument they soon discovered two new metals, cesium and rubidium, which they classified with sodium, potassium, and lithium, which had been previously discovered by Davy and Arfwedson. The spectroscopic discovery of thallium by Sir William Crookes and its prompt confirmation by C. A. Lamy soon followed. In 1863 F. Reich and H. T. Richter of the Freiberg School of Mines discovered a very rare element in zinc blende, and named it indium because of its brilliant line in the indigo region of the spectrum.

. . . . . .

Nur immer zu! wir wollen es ergründen,
In deinem Nichts hoff' ich das All zu finden (*1*).*

> *Thus there was for him nothing small or great in Nature. Every phenomenon embraced for him an endless diversity of factors, and in the yellow flame of an ordinary alcohol lamp whose wick was sprinkled with salt, he saw the possibility of accomplishing the chemical analysis of the most distant stars* (*2*).†

In 1758 Marggraf noticed the yellow color imparted to a flame by sodium salts and the lavender color imparted by potassium salts (*3*). In 1802 Dr. Wollaston examined the spectrum of a candle flame through a prism, and saw the discontinuous band spectrum (*4*), (*22*). He said (*33*):

> When a very narrow line of the blue light at the lower part of the flame is examined alone, in the same manner, through a prism, the spectrum, instead of appearing a series of lights of different hues contiguous, may be seen divided into five images, at a distance from each other. The 1st is broad red, terminated by a bright line of yellow; the 2nd and 3rd are both green; the 4th and 5th are blue, the last of which appears to correspond with the division of blue and violet in the solar spectrum. . .

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* *But go on! We want to fathom it.*
In thy nothing I hope to find the universe.

† *So gab es für ihn nichts Kleines oder Grosses in der Natur. Jede Erscheinung umfasste ihm eine unbegrenzte Mannigfaltigkeit von Faktoren, und in der gelben Flamme einer gewöhnlichen Weingeistlampe, deren Docht mit Salz bestreut war, sah er die Möglichkeit, die chemische Analyse der fernsten Gestirne auszuführen.*

In 1814 Josef Fraunhofer, a young German physicist who had had thorough training in the art of glassmaking, made an unusually fine prism, saw for the first time the dark lines in the sun's spectrum, and designated eight of the most prominent ones by letters (*3*), (*23*). Henry Fox Talbot (*24*), an English scientist, found that, with the aid of a prism, he could distinguish lithium from strontium,* even though the salts of both give red flames (*4*), (*26*), (*32*). He stated that the dark lines previously observed by Sir David Brewster (*33*) in the spectrum of light which had passed through vapors of nitrous acid were caused by absorption of light (*5*), (*25*). In 1854 David Alter of Freeport, Pennsylvania, showed that each element studied had its own spectrum (*53*), (*54*), (*56*). A few years later Kirchhoff and Bunsen firmly established the science of spectroscopic analysis.

Courtesy Bausch & Lomb Optical Co.

IN 1818 JOSEF FRAUNHOFER (1787–1826) EXHIBITED HIS NEWEST SPECTROSCOPE BEFORE COUNSELOR UTZSCHNEIDER AND MR. REICHENBACH, HIS PARTNERS IN THE GLASSWORKS AND OPTICAL ESTABLISHMENT AT BENEDICTBEUERN

He discussed with them his latest researches on the diffraction of light which had led him to the discovery of grating spectra, the exact measurement of wave-lengths, and a brilliant confirmation of the undulatory theory of light.

(*The above illustration is from a painting by Karla Fischer, 1909.*)

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* Strontium salts were very rare at that time, and Talbot was indebted to Faraday for the specimen he used.

Robert Bunsen was the son of a professor of modern languages at Göttingen, and was born in that city on March 31, 1811. After attending the academy at Holzminden he entered the University of Göttingen, and studied chemistry under Professor Stromeyer. At the age of twenty years he received his degree of doctor of philosophy. This does not mean that Bunsen was precocious, for, as Wilhelm Ostwald explains, students graduated at a much earlier age then than they do now.

Aided by a grant from the Hanoverian government, the youthful Bunsen broadened his scientific education by traveling, mostly on foot, through Germany, France, Austria, and Switzerland, and meeting the scientists of those countries. For three years he went about studying geological formations, visiting factories and mines, and meeting technical men and professors (*2*). In 1836 he succeeded Wöhler at the higher technical school at Cassel. After serving in similar positions at Marburg and at Breslau, he finally became Leopold Gmelin's successor at Heidelberg, where he taught for thirty-eight years, finally retiring at the venerable age of seventy-eight years (*2*), (*50*).

SIR DAVID BREWSTER
1781–1868

Scottish physicist famous for his researches on the absorption, reflection, refraction, and polarization of light, and on doubly refracting crystals. One of the founders of the British Association for the Advancement of Science. He invented the kaleidoscope and improved the stereoscope. His optical researches led to great improvement in the construction of lighthouses.

Courtesy W. A. Hamor

DR. DAVID ALTER
1807–1881

American physician, physicist, and inventor. He observed the spark spectra of various metals and gases and predicted that "the prism may also detect the elements in shooting stars, or luminous meteors."

BUNSEN'S OLD LABORATORY AT HEIDELBERG, NOW TORN DOWN

Bunsen's very first paper contained a discovery of great benefit to humanity, for he showed that freshly precipitated ferric hydroxide is an antidote for arsenic poisoning. His important and dangerous research on cacodyl was carried out at Cassel and Marburg. Since his laboratory at Cassel was not equipped with hoods, he wore a mask with a long tube leading to the fresh air. While he was investigating cacodyl cyanide, an explosion occurred which shattered the mask, destroyed the sight of his right eye, and nearly ended his life; yet, after he recovered from the resulting critical illness, he carried the research to a successful conclusion.

HEINRICH DEBUS
1824–1915
German chemist who taught for many years at Guy's Hospital, London, and at the Royal Naval College, Greenwich. He prepared pure purpurin, discovered glyoxylic acid, glyoxal, and glyoxaline, and reduced hydrocyanic acid to methylamine. He wrote a delightful biography of his professor, Robert Bunsen.

This serious accident made him very cautious. When one of his students, Heinrich Debus, once wished to use some mercuric fulminate in a research, Bunsen objected and said (*6*),

> When I came to Marburg, I found in the collection of preparations a glass-stoppered bottle containing an ounce or more of mercuric fulminate. I took the flask

and carried it to a nearby deep stone-quarry, and threw it in.

Bunsen made a thorough study of the gases of the blast furnace, and it was in this connection that he developed his famous methods of gas analysis. He invented the carbon-zinc battery, the grease-spot photometer, and the ice and vapor calorimeters, and perfected the Bunsen burner. After the famous eruption of Mount Hekla in 1845, he went with a Danish expedition to study the active hot springs and geysers of Iceland, and by careful thermometric measurements made at great risk, explained their action before any scientific description of the American geysers had been given (*7*), (*27*), (*57*).

GUSTAV ROBERT KIRCHHOFF
1824–1887

German physicist and physical chemist. Professor of physics at Heidelberg and Berlin. Independent discoverer of the Kirchhoff-Stewart law of radiation and absorption. He explained the Fraunhofer lines of the solar spectrum, and, with Bunsen, founded the science of spectroscopic analysis, and discovered the elements cesium and rubidium.

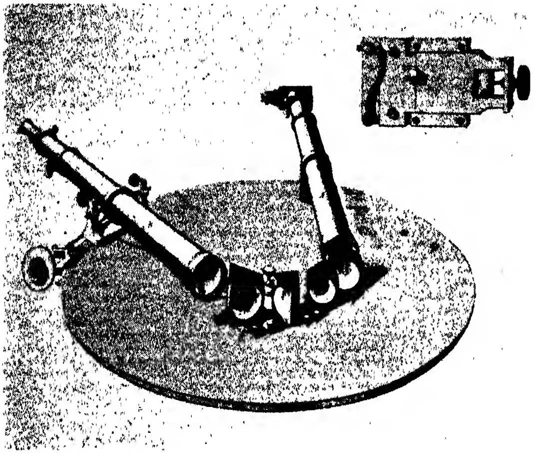
Cesium and Rubidium

Bunsen afterward carried out an elaborate series of photochemical researches with his lifelong friend, Sir Henry Roscoe, but suddenly discontinued this work. The reason for this may best be told in his own words as quoted from his letter to Roscoe written on November 15, 1859 (*7*):

> At present [said he] Kirchhoff and I are engaged in a common work which doesn't let us sleep. . . .Kirchhoff has made a wonderful, entirely unexpected discovery in finding the cause of the dark lines in the solar spectrum, and increasing them artificially in the sun's spectrum, and in producing them in spectra which do not have lines, and in exactly the same position as the corresponding Fraunhofer lines. Thus a means has been found to determine the composition of the sun and fixed stars with the same accuracy as we determine sulfuric acid, chlorine, etc., with our chemical reagents. Substances on the earth can be determined by this method just as easily as on the sun, so that, for example, I have been able to detect lithium in twenty grams of sea water.

Gustav Robert Kirchhoff, a young professor from Königsberg, Prussia, who had recently followed Bunsen from Breslau to Heidelberg, is generally regarded as Bunsen's greatest discovery of the Breslau period. Kirchhoff was born in Königsberg on March 12, 1824, the third son of a counselor of justice. When he was twenty-four years old, he became a member of the teaching staff at the University of Berlin. After serving for a time as professor extraordinary at Breslau, he went to Heidelberg in 1854, and collaborated with Bunsen for many years. In 1875, however, he left the scene of his brilliant achievements, and went back to Berlin to serve as professor of physics and to work with Helmholtz. He died on October 17, 1887, at the age of sixty-three years.

Kirchhoff's mind was more speculative than Bunsen's, he had greater fondness for pure mathematics, and he was thoroughly familiar with the researches of Newton, Fraunhofer, and Clausius (*8*), (*46*). He showed Bunsen that, instead of looking through colored glass to distinguish between similarly colored flames, he ought to use a prism to separate the light into its constituent rays (*9*). On this principle they developed the Kirchhoff-Bunsen spectroscope, an instrument which proved to be of supreme importance not only in chemical analysis, but also in the discovery of new elements (*28*).


THE KIRCHHOFF-BUNSEN SPECTROSCOPE

They noticed that when ordinary salt was sprinkled into the flame of a Bunsen burner, a yellow line was seen through the spectroscope in exactly the position formerly occupied by the dark double line of the sun's spectrum known as the D-line. Attempting then to observe the dark D-line and the bright sodium line simultaneously, by allowing sunlight and yellow sodium light to shine on the slit of the spectroscope at the same time, they were astonished to find that the dark line did not become yellow, but became darker than before. Kirchhoff was so puzzled by this that he spent the entire day and night trying to account for it, and finally succeeded in producing the dark D-line artificially. He did this by using, instead of sunlight, a luminous flame, which gives a continuous spectrum containing no dark lines, and then bringing the yellow sodium flame in front of the slit as before. Kirchhoff gave as his explanation the analogy of sympathetic vibrations. The white light from the luminous flame, upon passing through the sodium flame, lost those vibrations which correspond to the yellow lines; and therefore the spectrum contained a dark line at that place (*9*), (*34*).

On April 11, 1860, Bunsen wrote, "Don't be angry with me, dear Roscoe, if

I have still done nothing more on our photochemical work," and explained that he was searching for a new alkali metal (*9*). On November 6 of the same year he wrote again to Roscoe:

> I have been very fortunate with my new metal. I have fifty grams of the almost pure chlorplatinate, which I can easily make absolutely pure. To be sure these fifty grams were obtained from 600 hundredweights (quintals) of mineral water, whereby $2^1/_2$ pounds of lithium chloride were obtained as a by-product. Since I have a simple method of separating it, I find it widely distributed. I shall name it *cesium* because of its beautiful blue spectral line. Next Sunday I expect to find time to make the first determination of its atomic weight.

Bunsen had announced this discovery to the Berlin Academy of Sciences on May 10, 1860 (*8*).

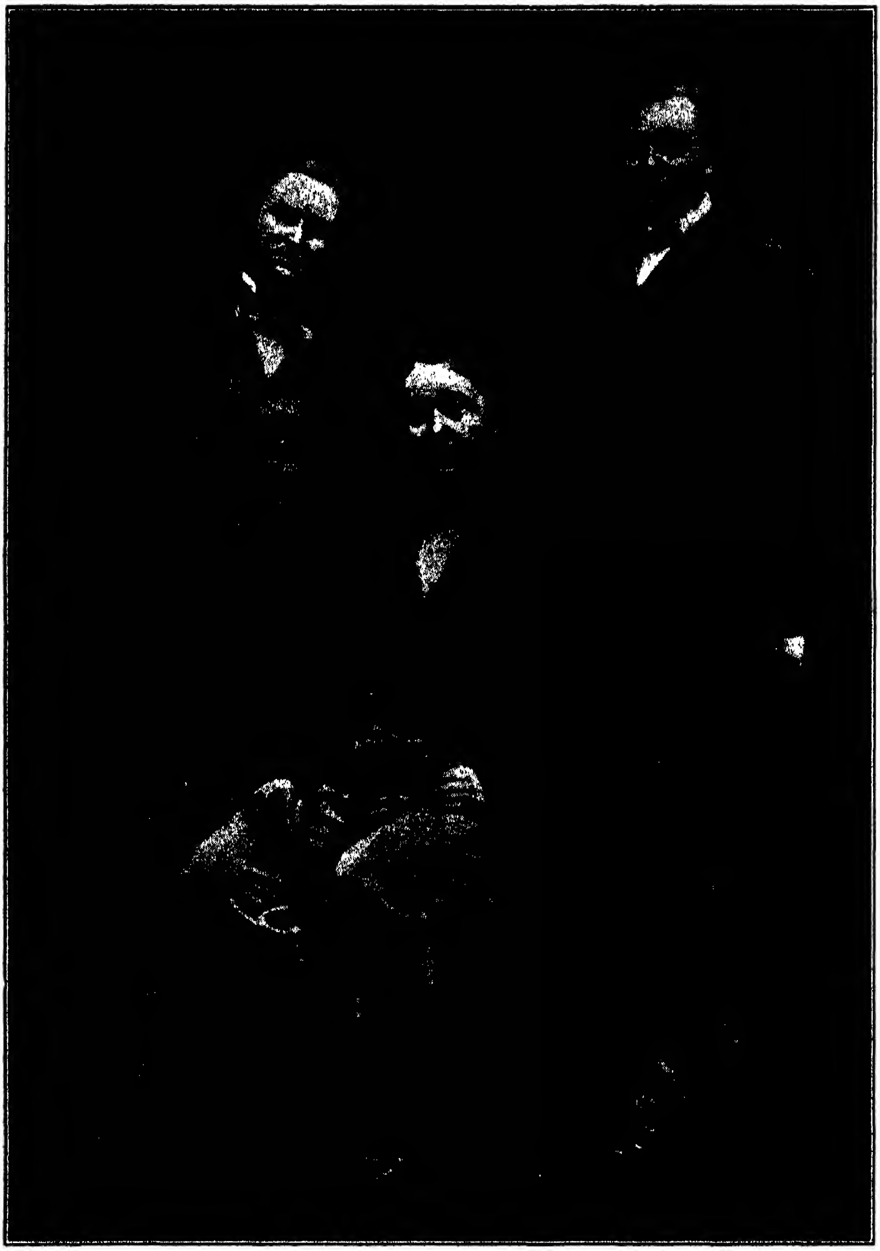
In one of their papers Bunsen and Kirchhoff told just how they traced down the new element:

> If one brings into the flame of the spectroscope a drop of mother liquor from the Dürkheim mineral water, one recognizes only the characteristic rays of sodium, potassium, lithium, calcium, and strontium. If then, after having precipitated by known methods the lime, strontia, and magnesia, one takes up the residue with alcohol previously treated with nitric acid to fix the bases, one obtains, after having removed the lithia by means of ammonium carbonate, a mother liquor which in the spectroscope gives the lines of sodium, potassium, and lithium, and, in addition, two remarkable blue lines, very close together, one of which coincides almost exactly with the line Sr δ.
>
> Now there is no simple substance known which gives two such rays in this part of the spectrum; one may therefore conclude the certain existence of a simple unknown substance, belonging to the group of alkali metals. We propose to give this new metal the name *cesium* (symbol Cs) from *caesius*, which the ancients used to designate the blue of the upper part of the firmament. This name seems to us to be justified by the facility with which one may confirm, by the beautiful blue color of the incandescent vapor of this new element, the presence of a few millionths of a milligram of this simple substance mixed with soda, lithia, and strontia (*4*), (*29*), (*30*).

From Muspratts's "Chemistry Theoretical, Practical, and Analytical"

ROBERT WILHELM BUNSEN
1811–1899

German chemist who investigated the cacodyl radical, the geysers of Iceland, and the chemical action of light. Inventor of the Bunsen battery, the grease-spot photometer, ice and vapor calorimeters, the thermoregulator, the constant-level water-bath, and the filter pump.



(*Left to right*) G. Kirchhoff, R. W. Bunsen, and H. E. Roscoe, in 1862

Kirchhoff and Bunsen invented the spectroscope and founded the science of spectroscopic analysis. Roscoe collaborated with Bunsen in photochemical researches, and was the first to prepare metallic vanadium.

Other chemists had examined cesium minerals before but had failed to recognize the presence of the new metal. Plattner in 1846 had analyzed som pollux from Elba, and had been unable to make his results total 100 per cent (*10*), (*36*). When Félix Pisani (1831–1920) examined it four years after the discovery of cesium, he found that Plattner had mistaken his cesium sulfate for a mixture of the sulfates of sodium and potassium (*8*), (*37*), (*58*).

On February 23, 1861, only a few months after the discovery of cesium, Bunsen and Kirchhoff announced to the Berlin Academy the existence of still another alkali metal. The report runs as follows:

> If one treats lepidolite from Saxony by one of the known methods which yield a solution of the alkalies separated from the other elements, and if one pours some platinic chloride into the liquid, one obtains an abundant precipitate which, tested in a spectroscope, shows only the lines of potassium.
>
> If one washes this precipitate several times with boiling water, and tests it at intervals in the apparatus, one notices two new lines of a magnificent violet located between the lines Sr δ and the Ka β† line of potassium As the washing is continued, these lines stand out more and more against the continuous spectrum of potassium, which fades away. Soon one sees a certain number of new rays in the red, the yellow, and the green. None of these lines belong to elements hitherto discovered. Among them we may mention especially two remarkable red lines just beyond the brilliant Fraunhofer line A, or, if one prefers, the brilliant K α line which corresponds to it, which ray is located at the extreme red end of the solar spectrum. The magnificent dark red color of these rays of the new alkali metal led us to give this element the name rubidium and the symbol Rb from ***rubidus***, which, with the ancients, served to designate the deepest red (*4*), (*30*), (*31*), (*35*).

CARL FRIEDRICH PLATTNER*
1800–1858

Professor of metallurgy at the Freiberg School of Mines. Author of books on blowpipe analysis and the roasting of ores. He was an expert analyst, trained under Heinrich Rose. When his careful analysis of pollux was made in 1846, the spectroscope had not yet been invented, and he was unable to recognize the presence of the new element cesium.

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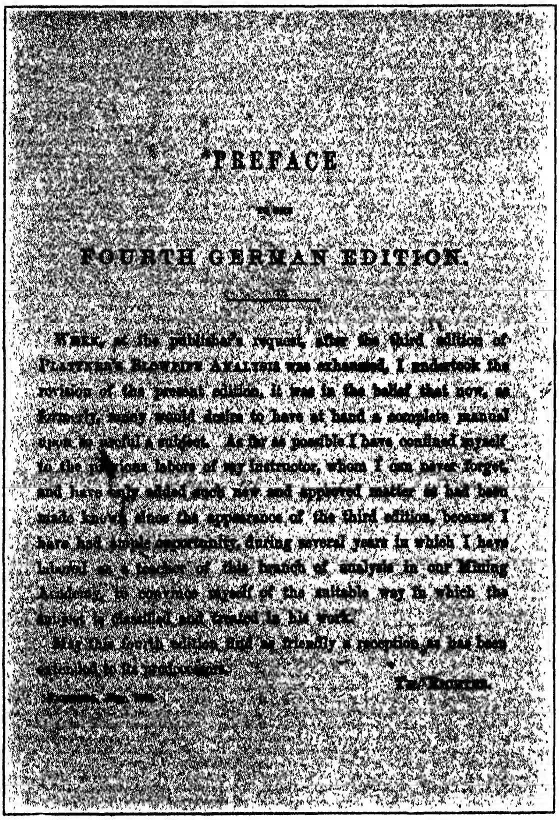
* The portrait of Plattner has been reproduced from F. G. Corning's "A Student Reverie" by kind permission of the author.

† Bunsen and Kirchhoff used the symbol *Ka* for potassium (***kalium***), instead of *K*.



PREFACE

TO THE

FOURTH GERMAN EDITION.

When, at the publisher's request, after the third edition of Plattner's Blowpipe Analysis was exhausted, I undertook the revision of the present edition, it was in the belief that now, as formerly, many would desire to have at hand a complete manual upon so useful a subject. As far as possible I have confined myself to the previous labors of my instructor, whom I can never forget, and have only added such new and approved matter as had been made known since the appearance of the third edition, because I have had ample opportunity during several years in which I have labored as a teacher of this branch of analysis in our Mining Academy, to convince myself of the suitable way in which the subject is classified and treated in his work.

May this fourth edition find as friendly a reception as has been extended to its predecessors.

The Editor.

[illegible]

PLATTNER'S "BLOWPIPE ANALYSIS" WAS REVISED BY HIS FORMER STUDENT, HIERONYMUS THEODOR RICHTER, WHO, WITH FERDINAND REICH, DISCOVERED THE ELEMENT INDIUM

The colorless flame of the burner which Bunsen perfected in 1854–5 made this research possible.

Although Bunsen succeeded in isolating rubidium (*42*), he observed cesium only by means of its spectral lines (*41*). Twenty years later Dr. Carl Setterberg succeeded in isolating cesium by electrolysis of the cyanide in presence of barium cyanide. The electrolytic part of the research was performed in Bunsen's laboratory.

When the five-hundredth anniversary of Heidelberg University was celebrated in 1886, an elaborate breakfast was served which lasted more than three hours. Bunsen fell asleep during one of the tiresome speeches, but at one place in the address the speaker's loud oratory caused the aged chemist to awake with a start. Rubbing his eyes, he whispered to his neighbor, "I thought I had let a test-tube full of rubidium fall to the floor"* (*11*).

On another occasion an Englishwoman, to whom he had just been introduced, mistook him for Josias Bunsen, the ambassador, and asked him if he had finished his book entitled "*Gott in der Geschichte.*" "Alas," replied Bunsen, "My untimely death prevented me"† (*11*).

Robert Bunsen was one of the most modest of men. When he found it necessary to mention his own discoveries in his lectures, he never said, "I have discovered," but always "*Man hat gefunden.*" However, when the

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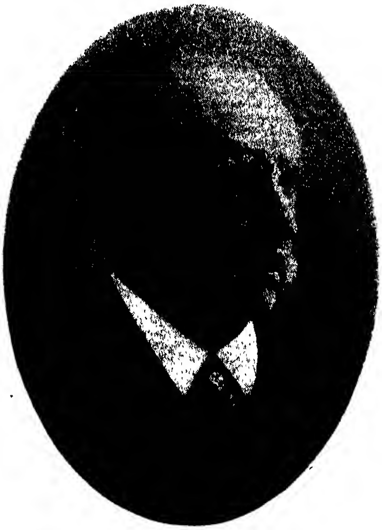
* *Mir war als hätte ich ein Probierröhrchen mit Rubidium auf den Boden fallen lassen.*

† *Ach daran hat mich ja mein frühzeitiger Tod verhindert.*

lecture dealt with spectral analysis, his students showed by prolonged applause that they understood and were proud of his great achievements. Bunsen won many honors and medals, but of these he once said sadly, "Such things had value for me only because they pleased my mother; she is now dead"* (*12*), (*49*).

Like Vauquelin and Cavendish, Bunsen never married, and, when asked for the reason, he used to say, "I never could find the time." Perhaps this lack of family ties made his students even more dear to him, for he used to work all day in the laboratory, patiently showing them the fine details of chemical manipulation. When he was seventy years old, he wrote to Roscoe, "In the years which I am rapidly approaching, one lives more in the recollection of past happy days than in the present; and to the most pleasure-giving of them belong those which for many years we spent in true friendship together." After his long day's work, his favorite recreation was to go walking over the chestnut-wooded hills near Heidelberg in company with a friend like Kirchhoff or Helmholtz (*13*).



HERMANN (LUDWIG FERDINAND) VON HELMHOLTZ, 1821–1894

Professor of physiology at Bonn and at Heidelberg. Professor of physics at Berlin. Inventor of the ophthalmoscope, an instrument for examining the retina of the eye. He expressed the principle of the conservation of energy in mathematical form.

Bunsen was blessed with a brilliant mind, a happy disposition, a strong, healthy body, and a long life (*48*). He was seventy-six years old when he invented the vapor calorimeter, and after he retired from his Heidelberg professorship at the age of seventy-eight, he still had ten years to live. These last days were brightened by the honor and respect paid him by his former students and colleagues. Sir Henry Roscoe said that during the peaceful sleep in which Bunsen lay for three days preceding his death on August 16, 1899, his face retained "the fine intellectual expression of his best and brightest days" (*13*).

After the brilliant researches of Bunsen and Kirchhoff had paved the way, other new elements were soon revealed by the spectroscope. Among these may be mentioned thallium, indium, gallium, helium, ytterbium, holmium, thulium, samarium, neodymium, praseodymium, and lutecium.

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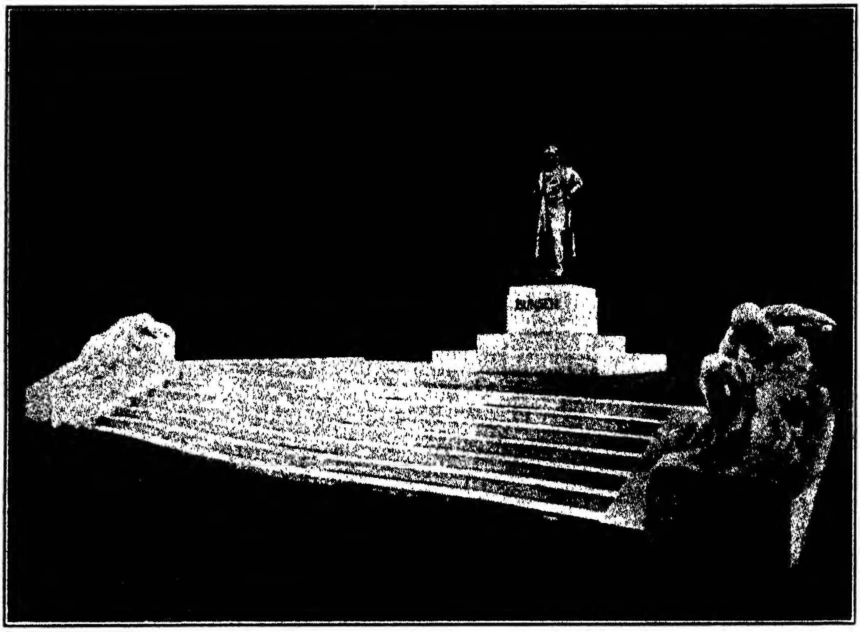
* *Solche Dinge hatten nur Werth für mich, weil sie meine Mutter erfreuten; sie ist nun todt.*



BUNSEN MEMORIAL IN HEIDELBERG

Thallium

The first indication of the existence of thallium was noted by Sir William Crookes. Sir William was born on June 17, 1832, and was educated in the grammar school at Chippenham. At the age of sixteen years he entered the Royal College of Chemistry, where Hofmann was serving as the first professor; yet in spite of the latter's inspiring influence, he never cared for organic chemistry. His first paper entitled "On the Selenocyanides" was published when he was nineteen years of age. In 1859 he started the publication of *Chemical News*, and until 1906 he was the sole editor of that important journal (*14*).

One day, very soon after Bunsen and Kirchhoff had announced their discovery of rubidium, Crookes happened to examine some residues from a sulfuric acid plant at Tilkerode in the Harz. Hofmann had given him these residues some years before, because they contained selenium compounds which could be converted into selenocyanides; and, after removing the selenium, Crookes had saved them because he thought they also contained tellurium.

When he examined the residues with the spectroscope, however, he found no lines of tellurium, and the lines of selenium soon faded out. Soon there appeared a beautiful green line that he had never seen before. He concluded that the material must contain a new element, and because of the green line in the spectrum he named it *thallium*, or *green branch*. His first announcement appeared in the *Chemical News* on March 30, 1861 (*38*). Although he at first believed thallium to be a non-metal similar to sulfur, he soon changed his mind, and in 1862 he was awarded a prize for some specimens labeled "Thallium, a new metallic element," which he exhibited at the International Exhibition (*14*).

From Muspratt's "Chemistry, Theoretical, Practical, and Analytical"

AUGUST WILHELM VON HOFMANN
1818–1892

German chemist who served for many years as the first professor at the Royal College of Chemistry in London Founder of the aniline dye industry. He was the first to prepare nitrobenzene and aniline from benzene He was one of the founders of the Deutsche Chemische Gesellschaft, and was elected president fourteen times.

Sir William Crookes will probably be longest remembered for his study of rarefied gases, and for his discoveries in radioactivity and molecular physics. After Sir William Ramsay discovered helium in 1895, it was Crookes who established its identity with the helium that Sir Norman Lockyer had observed spectroscopically in the sun's atmosphere. Crookes also invented the radiometer and the spinthariscope. While serving on the Glass Workers' Cataract Committee of the Royal Society, he carried out practical research of great humanitarian value. He prepared a kind of glass which, although nearly colorless, cut off the injurious rays from the white-hot molten glass, and protected the eyes of the workers (*14*). On two occasions Sir William visited the famous diamond mines at Kimberley, and in 1909 he wrote a little book on diamonds, which he dedicated to his wife.

The late Charles Baskerville once wrote a biographical sketch of Crookes, in which he gave the following pleasing description of his home (*15*):

> Sunday evenings Sir William is at home. Within his study walls, bebooked to the ceiling, one may find then the finest minds of science in England or in other lands, grappling in discussion with the unsolved problems, which oftentimes become no clearer than the increasing denseness of the tobacco smoke. Promptly at eleven o'clock there comes a bright rift in the clouds as Lady Crookes enters and charmingly leads all to the dining-room below. Punctilious in the performance of every duty, courteous but vigorous in argument, modestly assertive, learning from the youngest, Sir William draws out the humblest until he would become almost bold, yet, in return, he gives generously from his rich store of wide knowledge and large experience.

Courtesy Lyman C. Newell

SIR WILLIAM CROOKES

1832–1919

English physicist and chemist. Professor at the Royal College of Chemistry. Inventor of the radiometer and the spinthariscope. Founder and editor of *Chemical News*. He was the first to observe the green line of thallium and the first to prove the identity of solar and terrestrial helium. The discoverer of uranium X_1.

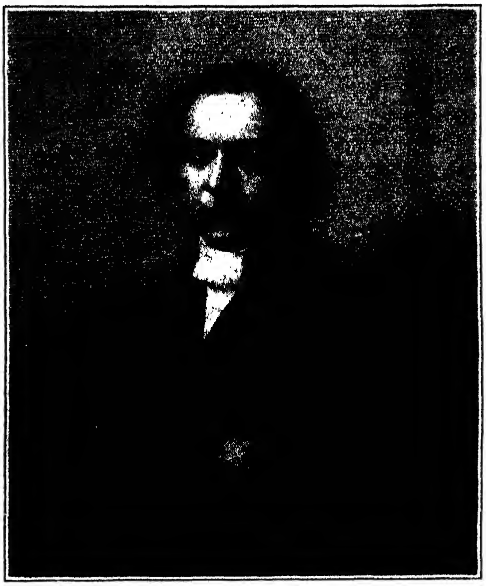
After Lady Crookes died in 1916 Sir William never recovered from his loss. He died on April 4, 1919, at the age of eighty-six years (*14*).

Although there seems to be no doubt that Sir William Crookes was the first to observe the green line of thallium, many chemical historians, especially the French ones, attribute the isolation of the metal itself to Claude-Auguste Lamy. He was born on July 15, 1820, at Néry in the Jura department of France, attended the École Normale Supérieure in Paris, and at the age of thirty-one years received his doctorate from Lille. He taught physics, first at Limoges and later at Lille (*16*).

In April, 1862, while he was a professor at Lille, he examined some slime from a sulfuric acid plant at Loos which was using Belgian pyrite, and observed the green line which had led Crookes to the discovery of thallium. Lamy's method of isolating thallium may best be described in his own words:

> When burned in suitable pits, pyrite yields, among other products, sulfur dioxide, arsenious and selenious acids, and the oxide of thallium, which are carried over into the first lead chamber, with the ferruginous dust. In this first chamber, especially if it has no other communication with the following ones than the gas pipe, the oxide of thallium deposits and accumulates, and finally thallium sulfate, with sulfates of lead, iron, and other foreign substances coming from the pyrite.
>
> The thallium [continued Lamy] is extracted from these deposits in the first chamber. When these deposits are heated almost dry, with approximately an equal volume of aqua regia, until the acid almost disappears, and the mass is then taken up with twice its weight of boiling water, one sees formed in the liquid as it cools an abundance of

yellow crystalline plates which, when purified by several successive recrystallizations, give a magnificent compound of thallium sesquichloride. When this chloride is submitted to the decomposing action of the electric current from four or five Bunsen cells, for example, there appears at the negative pole pure thallium. This is the experiment by which we have, for the first time, isolated the new metal (*17*), (*39*).



Courtesy Lyman C. Newell

JEAN-BAPTISTE-ANDRÉ DUMAS
1800-1884

Professor of chemistry at the Athenaeum and at the Sorbonne. He devised a method of determining vapor density, and developed the theory of types in organic chemistry, which he defended against Berzelius' dualistic electrochemical theory. From a study of the aliphatic alcohols, Dumas and Peligot developed the conception of homologous series.

Although Lamy claimed that Sir William Crookes's thallium was really a sulfide, the latter replied that he had prepared metallic thallium as early as May 1, 1862, but that because of its volatility he had not dared to melt the black powder to form an ingot (*18*). However, a committee from the French Academy, including Henri Sainte-Claire Deville, Théophile-Jules Pelouze, and J. B. A. Dumas, credited Lamy, rather than Crookes, with the isolation of thallium metal (*17*), (*40*).

After a careful study of the chemical compounds of the new metal, Professor Lamy concluded that it forms two series of salts, the thallous and the thallic, in which the metal is respectively mono- and trivalent. Since the thallous compounds resemble those of the alkali metals, whereas the thallic salts are similar to those of aluminum, Dumas once said, "It is no exaggeration to say that from the point of view of the classification generally accepted for the metals, thallium offers a combination of contradictory properties which would entitle one to call it the paradoxical metal, the ornithorhynchus of the metals"* (*40*), (*47*).

In 1865 Lamy became a professor of chemistry at the Central School of

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* *"Il n'y a pas d'exagération à dire qu'au point de vue de la classification généralement acceptée pour les métaux, le thallium offre une réunion de propriétés contradictoires qui autoriserait à l'appeler le métal paradoxal, l'ornithorynche des métaux."*

Arts and Manufactures at Paris. He published papers on magnetism, the progress of physics, the toxic effect of thallium, and the solubility of lime in water. He died at Paris on March 20, 1878 (*16*).

Indium*

FERDINAND REICH
1799–1882

Professor of physics and inspector at the Freiberg School of Mines. Discoverer of indium. He studied the deviations in the declination of the magnetic needle, the rainfall and snowfall in Freiberg, and the temperature of the rocks at different depths.

From "Cinquantenaire de la Société Chimique de France"

CLAUDE-AUGUSTE LAMY
1820–1878

President of the *Société Chimique de France* in 1873. The first person to prepare an ingot of metallic thallium. He made a thorough study of its compounds and proved that they are poisonous. Author of many papers on optics, electricity, pyrometry, organic and inorganic chemistry, and sugar technology.

In 1863 Ferdinand Reich, a professor of physics at the famous School of Mines at Freiberg, and his assistant, Hieronymus Theodor Richter, discovered the element indium. The former was born at Bernburg on February 19, 1799, and educated at Leipzig, Freiberg, Göttingen, and Paris.

In 1822 he went on foot to Göttingen to study chemistry under Stromeyer, whom he admired "because of his clarity and his appropriate choice of material" (*51*), and at the request of the Freiberg authorities he selected apparatus, minerals, and rare books for the Mining Academy. In the following year he was sent to Paris on a similar mission, and returned with platinum ware, certified

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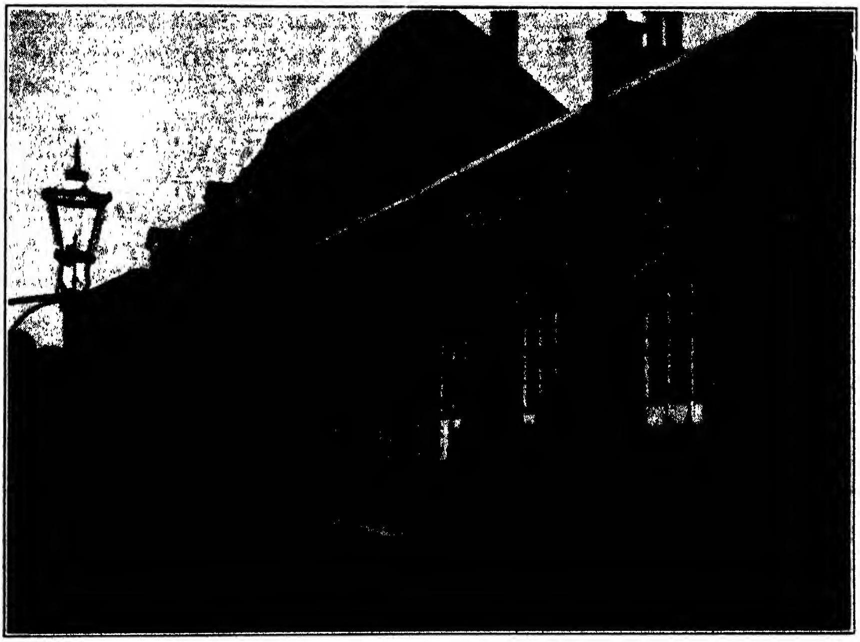
* The portraits of Reich and Richter and much of the information about indium have been obtained through the kind assistance of Professor L. W. McCay of Princeton University and Professor O. Brunck, Rector of the Freiberg Academy.

weights, apparatus, and minerals for the Freiberg Academy and for Stromeyer in Göttingen. While in Paris he studied at the Sorbonne, the School of Mines, and the Collège de France, and met Brongniart, Arago, Gay-Lussac, Thenard, Liebig, Élie de Beaumont, and Alexander von Humboldt. He especially admired Gay-Lussac "because of his modest simplicity, his thoroughness, and the wealth of his knowledge" (*51*).

From 1824 until his retirement in 1866 Reich served as inspector of the academy, and had charge of the mineral collections, purchase of supplies, keeping of records, cataloging of the library, and the editing of a mining and metallurgical calendar. He made an extended study of the deviations in the declination of the magnetic needle, and for many years kept an accurate record of the rainfall and snowfall in Freiberg. Soon after his return from Paris he began to lecture on the French system of weights and measures, and the metric system was first introduced into Saxony by Reich, Herder, and Brendel. Reich's observations of the temperatures of the rocks at different depths were of great scientific interest, and his results for the mean density of the earth were in good agreement with those of Cavendish.



CHEMICAL LABORATORY AT THE FREIBERG SCHOOL OF MINES

In the winter of 1830–31 Reich gave a continuation course of private lectures before about sixty educated citizens of Freiberg, most of whom were connected with the mines and smelters. Although these lectures added to his income, he discontinued them because they necessarily had to be less scientific than those designed for his regular students. For twelve years he also lectured on mineralogy, and for many years he had charge of the course in general chemistry.

Since Reich was always deeply concerned about the welfare of his students and set apart a special evening for entertaining them, they regarded him as a true friend. He occasionally gave private lectures in French for foreign students who had difficulty with the German language.

Smelter fumes which damaged crops, fodder, and stock were a serious problem. While Professor Carl Friedrich Plattner was studying means of removing sulfur dioxide, Reich devised a simple apparatus for determining the sulfur dioxide content of vapors and gases. Even the erection at Hilbersdorf of the tallest smokestack in Europe failed to overcome the difficulty, for the damage to fruits and trees then extended over a wider area than before. Although Professor Reich studied the fumes in forty smelters and chemical plants in Germany, Belgium, and England, the problem was not settled until after his death when in 1890 a tall smokestack was erected at Halsbrücke (*51*).

HIERONYMUS THEODOR RICHTER
1824–1898

Director of the Freiberg School of Mines. The first to observe the characteristic blue spectral lines of indium. Metallurgist, assayer, and authority on blowpipe analysis.

In 1863 Reich began a search for thallium in some Freiberg zinc ores from the Himmelsfürst mine consisting mainly of arsenical pyrites, blende, lead glance, silica, manganese, copper, and small amounts of tin and cadmium (*19*), (*43*). After roasting the blende to remove most of the sulfur and arsenic, he decomposed it with hydrochloric acid (*47*). When Clemens Winkler, who was then a metallurgist in the Saxon smalt works, visited Professor Reich in 1863, the latter showed him a straw-yellow precipitate and said, "This is the sulfide of a new element" (*52*). Because of his colorblindness, however, Reich entrusted the spectroscopic examination to his assistant, Richter.

Hieronymus Theodor Richter was born at Dresden on November 21, 1824. He became a metallurgical chemist at the Freiberg School of Mines. When he placed some of the zinc blende in the loop of a platinum wire and heated it in the flame of a Bunsen burner, he observed a brilliant indigo line which did not coincide with either of the blue lines of cesium (*20*), (*52*). Because of this characteristic spectral line the new element was christened *indium*. The publication of this contribution under joint authorship was a mistake which Professor Reich afterward regretted, for Richter tried to make it appear that he was the sole discoverer (*20*), (*51*), (*52*).

Reich and Richter found later that there are two indium lines, the brighter one being slightly more refrangible than the blue line of strontium, and the weaker one still more refrangible and located near the blue line of calcium. Indium compounds impart such a brilliant indigo-violet color to the Bunsen flame that they can be recognized even without a spectroscope.

They separated the chloride and the hydrated oxide of indium in small amounts, and, by cautiously heating a mixture of indium oxide and sodium carbonate on charcoal by means of a blowpipe, they also obtained some impure metal (*21*), (*43*). Metallic indium is a white, ductile, easily fusible metal like tin, and it leaves a mark when drawn across paper.

Reich and Richter found that it is easier to isolate it from the zinc than from the original blende. They reduced indium oxide in a current of hydrogen or illuminating gas and melted the metal under potassium cyanide (*44*), (*45*). At the suggestion of Ferdinand Reich, Clemens Winkler made a thorough study of the metal and its compounds (*20*).

In Wells' "Annual of Scientific Discovery" one finds an interesting description of the first metallic indium:

> Two specimens of indium were exhibited at the Académie des Sciences in April, 1867, by Richter. They were prisms, each about four inches long, the section being that of a trapezium with a height of one-half inch and with bases respectively $^1/_2$ inch and $^3/_4$ inch in breadth. The metal was very pure and resembled cadmium; and Richter valued these two specimens at £800 (*21*).

Professor Reich took no part in political life, and his excellent library contained no books on that subject. For a few years, however, he served as commissioner of the poor, and always acted for the best interests of those in need. Although he had no children of his own, Reich helped to support and educate the eleven children of his unfortunate brother Ludwig, who had lost both wife and fortune. Some of the nieces lived for years at the home of Professor and Mrs. Reich, and one nephew received his gymnasium and university education through their generosity (*51*).

Reich loved to travel, and even in his boyhood days he kept a detailed diary of all his trips. After his retirement at the close of 1865 he bought a little house, where he lived for more than twenty years, spending much time with his scientific journals and books. After the death of his wife in 1876, a grandniece kept house for him until his death on April 27, 1882.

In 1875 Richter became director of the Freiberg School of Mines. His American student, LeRoy Wiley McCay, describes him as "a nervous, high-strung, mobile little man." He was expert in metallurgy and assaying, and revised some of the later editions of Plattner's "Blowpipe Analysis." One of his papers was on the extraction of gold from gold ores with chlorine water. He was most exacting with his students, who, nevertheless, enjoyed his unfailing good humor and bright flashes of wit (*20*). Richter died at Freiberg on September 25, 1898 (*16*).

Through the efforts of W. S. Murray and Daniel Gray, indium is now available commercially (*55*).

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XXI. THE PERIODIC SYSTEM OF THE ELEMENTS

Before continuing the story of the discovery of the chemical elements, it will be necessary to outline the early attempts at classification made by Döbereiner, Beguyer de Chancourtois, and Newlands, and to discuss briefly the periodic system of the elements which was developed independently by Lothar Meyer and Mendeléeff. This classification enabled Mendeléeff to predict the properties of a number of undiscovered elements and of their compounds with surprising accuracy, and proved to be of great assistance in all subsequent discoveries of new elements.

. . . . . .

Refrain from illusions, insist on work and not words,
patiently search divine and scientific truth (*1*), (*15*).

Wer ruft das Einzelne zur allgemeinen Weihe,
Wo es in herrlichen Accorden schlägt? (*2*)*

Although the alkali metals and the spectroscope aided greatly in revealing hidden elements, each new discovery was an unexpected event. Before the periodic law was discovered by Lothar Meyer and Mendeléeff in 1869, there was no way to predict what elements lay undiscovered nor to foretell their physical and chemical properties.

One of the important steps leading up to this great generalization was the discovery by Professor Johann Wolfgang Döbereiner of Jena of his famous triads (*10*), (*11*). He was born in December, 1780, the son of a coachman at Hof, near Bayreuth. On a foundation of only meager elementary instruction, practical training in various pharmacies, and attendance at a few lectures on philosophy, chemistry, botany, mineralogy, and languages, he developed such great ability for original research in chemistry that in 1810 A. F. Gehlen, the editor, and Duke Carl August made him professor

From Chemnitius' "Die Chemie in Jena von Rolfinck bis Knorr"†

JOHANN WOLFGANG DÖBEREINER
1780–1849

Professor of chemistry at Jena. His discovery of the *triads* was an important step toward the systematic classification of the chemical elements. He wrote many books and papers on general and pharmaceutical chemistry, mineral waters, the manufacture of vinegar, and the use of platinum as a catalyst. The original of this portrait is in the City Museum at Jena.

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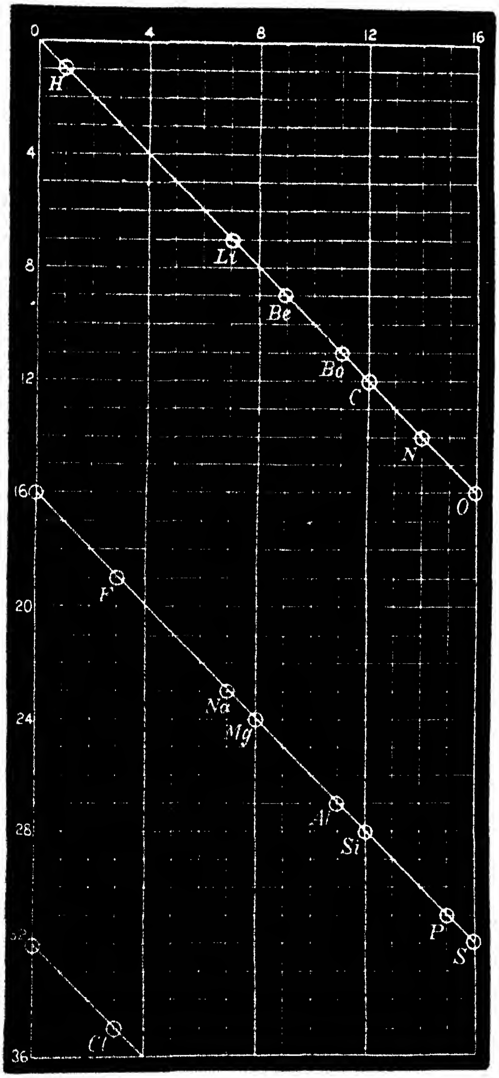
* *Who calls the individual to the universal consecration, where it vibrates in glorious harmony?*

† Reproduced by courtesy of Dr. Fritz Chemnitius.



A PORTION OF THE TELLURIC SCREW OF BEGUYER DE CHANCOURTOIS

extraordinary of chemistry at Jena (*22*). His personal and intellectual qualities soon won the high esteem of the Duke and the poet Goethe (*23*), (*24*), (*27*).

Döbereiner noticed in 1829 that there are several *triads* in which the middle element, that is, the one whose atomic weight lies midway between those of the other two, has properties which likewise are a mean of those of the other elements of the triad (*29*), (*31*).

Professor Döbereiner also made a thorough investigation of the catalytic action of platinum,* and wrote books on general and pharmaceutical chemistry, on the manufacture of vinegar, and on mineral waters for therapeutic purposes. Even before the time of Liebig, he gave practical laboratory instruction in analytical chemistry. He died on March 24, 1849.

Alexandre E. Beguyer de Chancourtois (1820–86), a professor of geology in the School of Mines in Paris, made in 1862 a "telluric screw," or helix, on a vertical cylinder, on which he placed the symbols of the elements at heights proportional to their atomic weights. He plotted the atomic weights as ordinates on the generatrix of a cylinder the circumference of which, since the atomic weight of oxygen is 16, he divided into sixteen equal parts. He then traced on the surface of the cylinder a helix making a 45° angle with the axis. The spiral therefore

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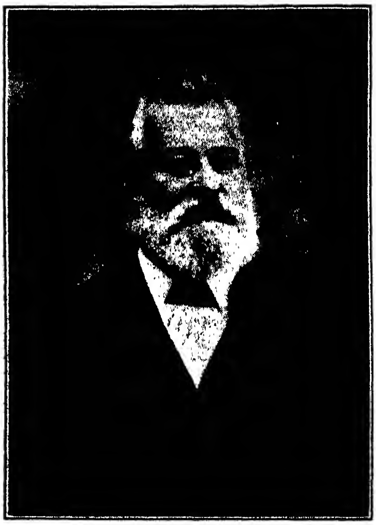
* Döbereiner was assisted for a time by Gottfried Wilhelm Osann, whose researches on platinum led to the discovery of ruthenium by Klaus.

crossed a given generatrix at distances from the base which were a multiple of 16. Thus lithium, sodium, and potassium, with atomic weights of 7, 23, and 39, respectively, fell on one perpendicular, whereas oxygen, sulfur, selenium, and tellurium fell on another.

Beguyer de Chancourtois observed the great similarity existing between elements appearing on the same generatrix, mentioned the periodic recurrence of properties, and stated that "the properties of substances are the properties of numbers." He presented to the French Academy a lithograph and a model of his "telluric screw" (*12*), (*13*), (*14*). Unfortunately, his heavy, obscure literary style, his use of terms more familiar to geologists than to chemists, and the failure of the *Comptes rendus* to publish a reproduction of his diagram all contributed to a lack of appreciation of his contribution† (*19*).



JOHN ALEXANDER REINA NEWLANDS*
1837–1898

Professor of chemistry at the School of Medicine for Women and at the City of London College. Discoverer of the law of octaves. He was an authority on the chemistry of sugar refining.

Another important advance in the classification of the elements was made by John Alexander Reina Newlands. He was born in Southwark, England, in 1837, and was educated privately by his father, a minister of the Established Church of Scotland. When he was nineteen years old he entered the Royal College of Chemistry to study under Hofmann. His sympathy for Italy, the land of his maternal ancestors, led him to volunteer in 1860 for military service under Garibaldi. When Italian freedom had been won he returned to London, practiced for a time as an analytical chemist, and taught at the Grammar School of St. Saviour's, Southwark, at the School of Medicine for Women, and at the City of London College. For many years he was the chief chemist in a large sugar refinery at Victoria Docks, and with his brother, Mr. B. E. R. Newlands, he afterward published a treatise on sugar.

In 1864 he arranged the elements in the order of increasing atomic weights, and noticed that after each interval of eight elements, similar physical and chemical properties reappeared (*16*). Thus he divided them

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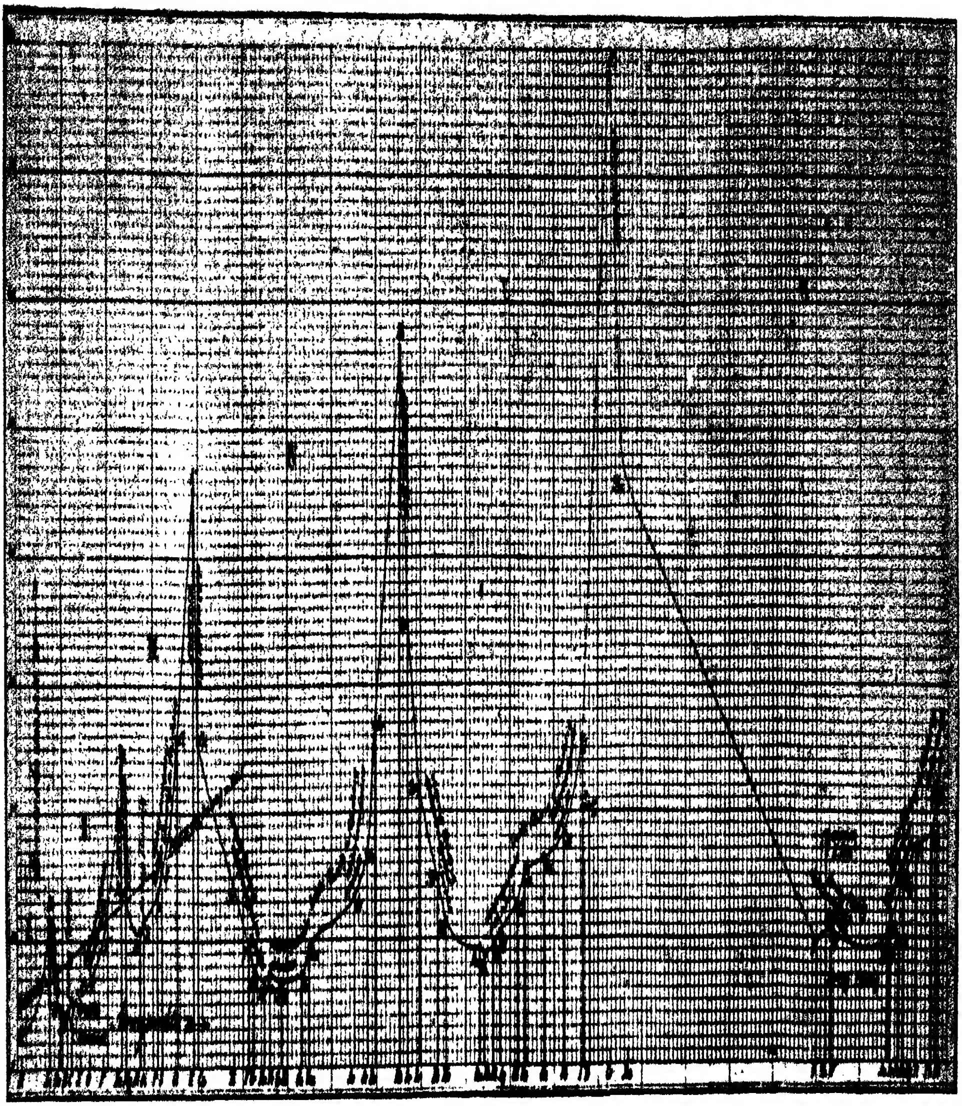
* This portrait was obtained through the courtesy of Mr. R. B. Pilcher, Registrar and Secretary of the Institute of Chemistry of Great Britain and Ireland.

† The *Comptes rendus* finally published it, however, nearly thirty years later. See ref. (*35*).

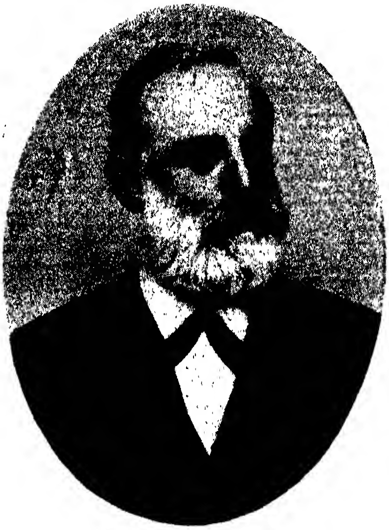


Lothar Meyer's Periodic Curve of Atomic Volumes

Atomic volumes are plotted as ordinates, atomic weights as abscissae.

into natural families and periods, but for this law of octaves he gained nothing but public ridicule from the English Chemical Society. So little was the importance of atomic weights realized that a certain wag once asked him if he could not get the same result by arranging the elements according to the initials of their names (*3*), (*18*). The Chemical Society refused to publish his paper, but in 1887 the Royal Society awarded him the Davy Medal for it (*9*), (*17*).

In a biographical sketch in *Nature*, W. A. T. (Tilden?) stated that this tardy recognition, which came five years after the same honor had been conferred on Mendeléeff and Lothar Meyer, did not do Newlands full justice. "If Newlands had been a Frenchman," said he, "the Academy of Sciences and the Chemical Society, even if they had at first fallen into error, would have taken care that in the distribution of honours their own countryman should not come in last" (*36*). Nevertheless, Newlands kept up his regular attendance at the meetings of the Chemical Society and won many friends by his kindness and courtesy. He died of influenza on July 29, 1898.

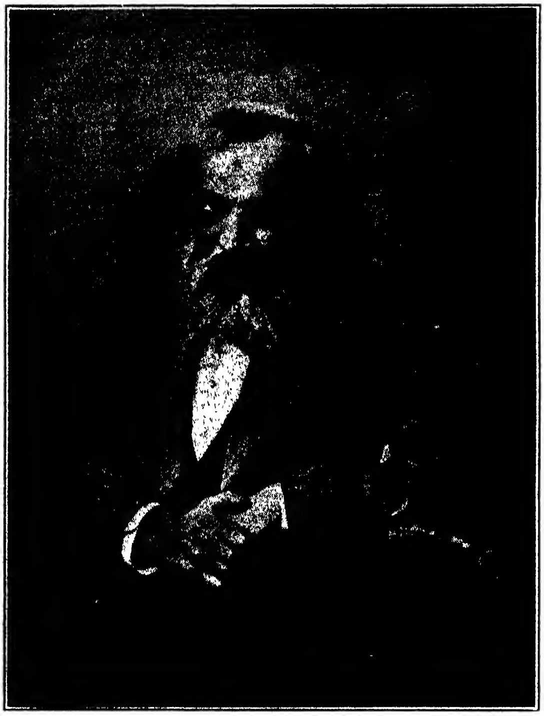


(JULIUS) LOTHAR MEYER
1830–1895

German chemist and physician. Professor of chemistry at Breslau and at Tübingen. Co-discoverer with Mendeléeff of the periodic system of the elements. Some of his researches were on the gases of the blood, the molecular volumes of chemical compounds, atomic weights, a sensitive thermoregulator, the paraffins, and the constitution of fuchsine.

The periodic system of the elements was developed independently and almost simultaneously by Lothar Meyer in Germany and Mendeléeff in Russia. Julius Lothar Meyer was born on August 19, 1830, at Varel on the Jade in the Grand Duchy of Oldenburg. His father was a physician, and his mother used to assist at operations. Both of the sons received a medical education, but Lothar became a chemist and Oskar Emil a physicist. Since Lothar was not a robust child, he was given an out-of-door education under the guidance of the chief gardener at the Grand Duke of Oldenburg's summer palace at Rastede. By this means he developed not only a sturdy body, but also an abiding interest in Nature. He received his degree of doctor of medicine from Würzburg University in 1854 (*33*).

Meyer knew by this time that he was more interested in research than in the practice of medicine. Therefore, he went to Heidelberg to study under



DMITRI IVANOVICH MENDELÉEFF
1834–1907

Professor of chemistry at the University of Petrograd. Author of the "Principles of Chemistry," a remarkable textbook. He studied the important oil fields of Russia and the United States. The periodic system of the elements was discovered independently by Mendeléeff in Russia and Lothar Meyer in Germany.

Bunsen and Kirchhoff, where the latter soon aroused in him an intense interest in applied mathematics. In 1858 Lothar Meyer became a privatdocent in physics and chemistry at Breslau, and six years later his brother Oskar Emil joined him there as professor of mathematics and mathematical physics. Lothar Meyer's book, "Moderne Theorien der Chemie," which was published in the same year and which contained his first incomplete periodic table, made his name well known throughout the scientific world (*4*).

In 1868 he went to the *Carlsruhe Polytechnicum*, which, during the war between France and Germany, was used as an army hospital. Here he made good use of his medical training, and rendered such valuable service as army surgeon that, at the close of the war, he was awarded a medal (*4*).

In December, 1869, he arranged fifty-six elements in a table consisting of groups and sub-groups (*26*), (*30*). He also drew a curve showing the relation between the atomic weights and the atomic volumes of the elements, and found that this is divided by maxima into six sections. In the second and third sections the atomic weight increases by increments of sixteen units, but in the fourth and fifth sections the atomic weight increments are much larger: about forty-six units each. He then prepared other curves which showed that fusibility, volatility, malleability, brittleness, and electrochemical behavior are also periodic properties. The volatile and easily fusible elements lie on the ascending portions of the curves, whereas the refractory elements are on the descending portions or at the minima.

In 1876 Lothar Meyer became a professor of chemistry at the University of Tübingen. He served the university devotedly in this capacity and as rector, and his fame and ability attracted students from all parts of the world (*4*). He died on April 11, 1895.

Dmitri Ivanovich Mendeléeff was born in Tobolsk in western Siberia on February 8, 1834. He was of Russian and Mongolian descent, and was the youngest child in a very large family. Some biographers mention seventeen children, but Mendeléeff's personal friend, the late Dr. Brauner, stated that there were fourteen (*37*).

Maria Kornileff Mendeléeff was especially fond of her youngest child, Dmitri, and called him by the affectionate name, Mitjenka (*15*). While Mitjenka was still very young, his father, who was the director of the Tobolsk gymnasium, lost his sight because of cataracts in both eyes. Although the government granted him a pension of one thousand roubles (about $500), this would not begin to feed and clothe his large family. It therefore fell to the lot of Maria Mendeléeff not only to care for her poor, blind husband and her eight children who were still dependent, but also to undertake a business career. The Kornileff family had founded the first glassworks and paper mill in Tobolsk, and Maria Mendeléeff now established in the neighboring village of Axemziansk her own glassworks, which she directed as an efficient and successful executive while carrying her heavy household burdens (*9*), (*21*), (*37*).

HENRI VICTOR REGNAULT
1810–1878

French chemist and physicist. He made precise measurements of specific heats and heats of fusion and vaporization, and of the velocity of sound, and contributed to the theory of organic radicals. Among his students may be mentioned Cannizzaro, Kekulé, and Mendeléeff.

As a child, Dmitri excelled in mathematics, physics, and history, but he never liked Latin. His first science teacher was his brother-in-law, Bassargin, a well-educated Russian who had been exiled for attempting to start a revolution (*9*), (*25*). Bassargin was one of the "Decembrists" who in December, 1825, made an unsuccessful attempt to overthrow the Emperor Nicholas I.

Dmitri completed the gymnasium course at the age of sixteen years, but shortly before his graduation a profound double tragedy had occurred. His helpless father had died of tuberculosis, and the glassworks had burned to the ground. Maria Mendeléeff, then fifty-seven years old, secured horses and started out with her two youngest children for Moscow, hundreds of miles away. Unable to enroll Dmitri in the university because of insufficient political influence, she went to Petrograd to interview Pletnoff, the director of the Central Pedagogic Institute and friend of her late husband, who succeeded in obtaining financial aid from the government and in making it possible for Dmitri to begin his work in the department of physics and mathematics (*34*).

TABLE II.

THE ATOMIC WEIGHTS OF THE ELEMENTS

Distribution of the Elements in Periods

Groups	Higher Salt-forming Oxides	Typical or 1st small Period	Large Periods				
			1st	2nd	3rd	4th	5th
I.	R_2O	Li = 7	K 39	Rb 85	Cs 133	—	—
II.	RO	Be = 9	Ca 40	S 87	Ba 137	—	—
III.	R_2O_3	B = 11	Sc 44	Y 89	La 138	Yb 173	—
IV.	RO_2	C = 12	Ti 48	Zr 90	Ce 140	—	Th 232
V.	R_2O_5	N = 14	V 51	Nb 94	—	Ta 182	—
VI.	RO_3	O = 16	Cr 52	Mo 96	—	W 184	Ur 240
VII.	R_2O_7	F = 19	Mn 55	—	—	—	—
VIII.			Fe 56	Ru 103	—	Os 191	—
			Co 58·5	Rh 104	—	Ir 193	—
			Ni 59	Pd 106	—	Pt 196	—
I.	R_2O	H = 1. Na = 23	Cu 63	Ag 108	—	Au 198	—
II.	RO	Mg = 21	Zn 65	Cd 112	—	Hg 200	—
III.	R_2O_3	Al = 27	Ga 70	In 113	—	Tl 204	—
IV.	RO_2	Si = 28	Ge 72	Sn 118	—	Pb 206	—
V.	R_2O_5	P = 31	As 75	Sb 120	—	Bi 208	—
VI.	RO_3	S = 32	Se 79	Te 125	—	—	—
VII.	R_2O_7	Cl = 35·5	Br 80	I 127	—	—	—
		2nd small Period	1st	2nd	3rd	4th	5th
			Large Periods				

From Mendeléeff's "Principles of Chemistry," Vol. 1

MENDELÉEFF'S PERIODIC TABLE OF THE ELEMENTS

The groups are arranged horizontally instead of vertically.

A few months later Maria Mendeléeff laid down her heavy burdens, consoled in her last hours by the thought that her Dmitri was, after all, to have an education. Some years later he wrote in the preface to his famous book on solutions:

> This investigation is dedicated to the memory of a mother by her youngest offspring. Conducting a factory, she could educate him only by her own work. She instructed by example, corrected with love, and in order to devote him to science she left Siberia with him, spending thus her last resources and strength. When dying, she said, "Refrain from illusions, insist on work, and not on words. Patiently search divine and scientific truth." She understood how often dialectical methods deceive, how much there is still to be learned, and how, with the aid of science without violence, with love but firmness, all superstition, untruth, and error are removed, bringing in their stead the safety of discovered truth, freedom for further development, general welfare, and

inward happiness. Dmitri Mendeléeff regards as sacred a mother's dying words. October, 1887 (*1*).

When Mendeléeff graduated from the Pedagogical Institute, he received a gold medal for excellence in scholarship. Between 1859 and 1861 he worked with Regnault in Paris and with Bunsen in Heidelberg. Upon returning to Petrograd in 1861, he was granted his doctorate and was appointed professor of chemistry at the Technological Institute. Eight years later he became the professor of general chemistry at the University of Petrograd.

J. Heyrovský, Collection Czechoslov. Chem. Communications

DMITRI MENDELÉEFF AND BOHUSLAV BRAUNER IN PRAGUE, 1900

The latter was a professor of chemistry at the Bohemian University of Prague. He wrote a charming biographical sketch of his friend, Mendeléeff, who once had the portraits of Lecoq de Boisbaudran, Nilson, Winkler, and Brauner framed together because they had contributed most toward the development of his periodic system (*40*).

In March of the same year he presented to the Russian Chemical Society his famous paper on "The Relation of the Properties to the Atomic Weights of the Elements." Mendeléeff's great merit as a discoverer lay in the boldness with which he asserted that the atomic weights of certain elements which did not fit into his system had been incorrectly determined, and that new elements would some day be discovered to fit into the vacant spaces in the periodic table (*30*), (*32*). He even predicted the properties of a number of these undiscovered elements, and three of them, which he called ekasilicon, ekaboron, and ekaaluminum, were discovered during his lifetime, and are now known, respectively, as germanium, scandium, and gallium.* Thus he was able to say in his Faraday lecture in 1889: "The law of periodicity first enabled us to perceive undiscovered elements at a distance which formerly was inaccessible to chemical vision; and long ere

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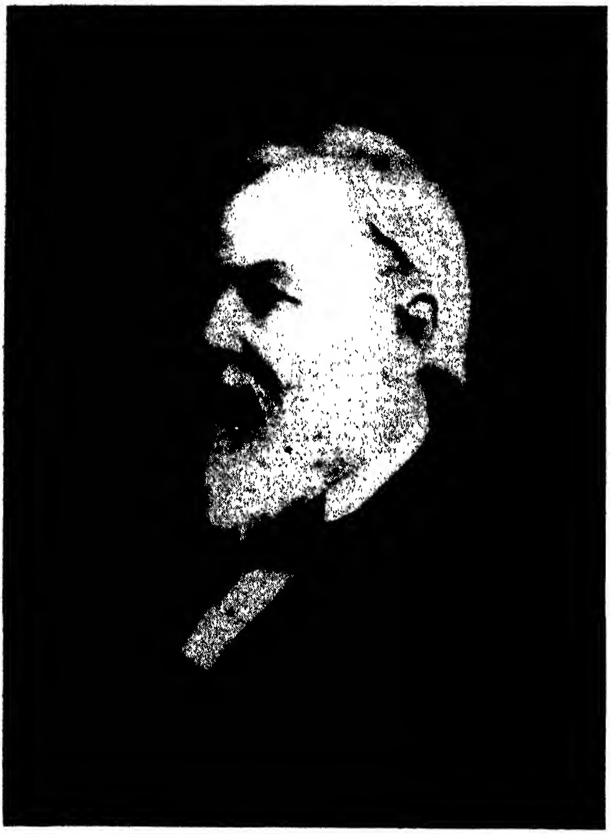
* See Part XXII, pp. 399–413.

they were discovered, new elements appeared before our eyes possessed of a number of well-defined properties" (*5*), (*20*), (*28*). Mendeléeff's periodic table (*6*) was more complete than any of the preceding ones, and more thoroughly founded on experiment.

He willingly recognized Lothar Meyer's claim to independent discovery. He was asked to speak before the British Association in Manchester in 1887, but, feeling unable to address the assembly in English, he simply rose and bowed. Lothar Meyer then rose to thank the English scientists for their hospitality and, fearing lest a wrong impression be made, began with the modest words, "I am not Mendeléeff. I am Lothar Meyer." He also was greeted with generous applause. In 1882 the Davy Medal had been awarded jointly to Mendeléeff and Meyer (*7*).



Courtesy of the College of Charleston

LEWIS REEVE GIBBES
1810–1894

Professor of chemistry and other sciences at the College of Charleston. He published many scholarly papers on chemistry, astronomy, zoölogy, and geology.

TABLE OF CHEMICAL ELEMENTS.

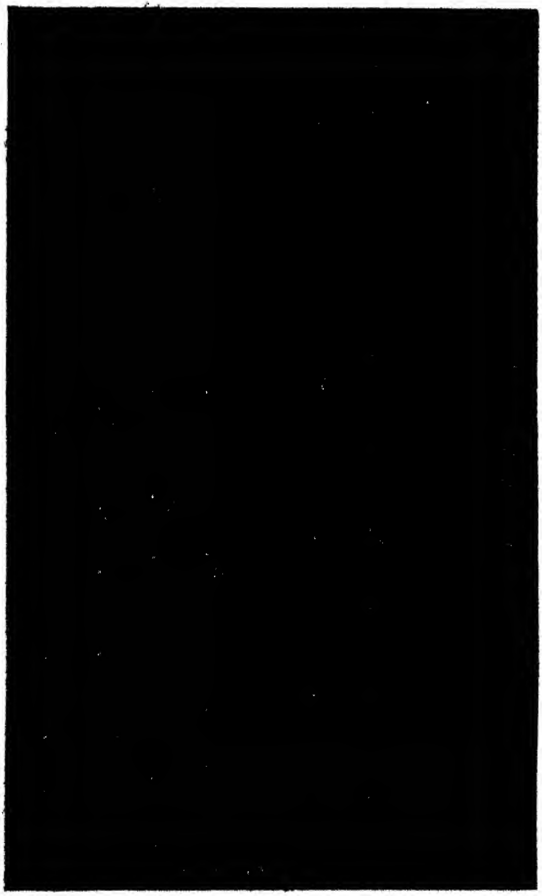
a	SERIES.									GROUPS.
	A	B	C	D	E	F	G	H, I	K	
−4		C=12	Si=28	Ti=50			Sn=118			Silicon Gr.
−3		N=14	P=31	V=51.3	As=75	Cb=94	Sb=122	Ta=182	Au=196.6	Phosphorus Gr.
−2		O=16	S=32	Cr=52.5	Se=79	Mo=96	Te=128	W=184	Os=199	Sulphur Gr.
−1		F=19	Cl=35.5		Br=80		I=127			Chlorine Gr.
0										
+1	Li=7	Na=23	K=39		Rb=85	Ag=108	Cs=133		Tl=204	Kalium Gr.
+2	Gl=9.3	Mg=24	Ca=40	Zn=65	Sr=87.5	Cd=112	Ba=137		Pb=207	Calcium Gr.
+3	−B=11								Bi=210	
	Al=27.5——	Cr=52.5 ;Mn=55 ;	Fe=56 ;	Co=59 ;	Ni=59 ;	Cu=63.5——	U=120			Iron Gr.
	Y=61.7			Zr=89.5;Ce=92 ; La=92 ; D=96				Er=112 ;	Th=115.7	
	In=74				Ru=104;Ro=104;Pd=106——			Pt=197 ;	Ir=197	Platinum Gr.
					H=1	Hg=200				

Courtesy Wendell H. Taylor

GIBBES' SYNOPTICAL TABLE (1875)

Mendeléeff and his students contributed to all branches of chemistry, and his literary work was also of great value. His textbook, "Principles of Chemistry," although hastily written, was the best chemistry text in the Russian language, and for this reason the Petrograd Academy awarded him the Demidoff prize. It is written in a peculiar style, with the footnotes occupying more space than the portion of the text in large type; yet, in spite of its strange appearance, it is a great chemical classic. He also investigated the Baku oil fields, the naphtha springs in the Caucasus, and the Pennsylvania oil fields (*8*), (*38*).

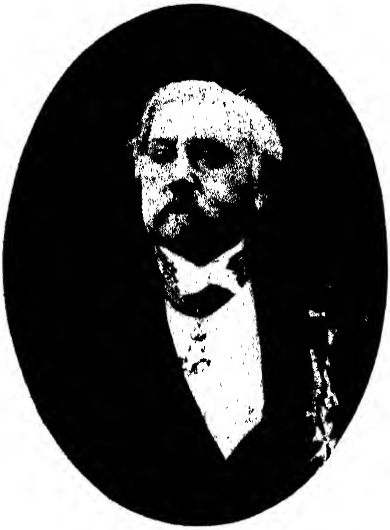
Mendeléeff had a keen appreciation of art and literature. He sometimes



Courtesy Wendell H. Taylor

GIBBES' DIAGRAM (1875)

wrote articles on art, and his study was furnished with pencil sketches of Lavoisier, Newton, Descartes, Galileo, Copernicus, Graham, Mitscherlich, Rose, Chevreul, Faraday, Dumas, and Berthelot drawn by his wife. His favorite author was Jules Verne, and his chief consolation during his last illness was the reading of "The Journey to the North Pole" (*9*), (*25*). He died of pneumonia on Saturday, February 2, 1907, and in a telegram to the widow, Czar Nicholas said, "In the person of Professor Mendeléeff, Russia has lost one of her best sons, who will ever remain in our memory" (*5*).



ALEXANDRE-EMILE BEGUYER DE CHANCOURTOIS
1820–1886

Inspector-general of mines and professor of geology at the *École Supérieure des Mines* in Paris. He made geological explorations in France, Asia Minor, Iceland, and Greenland. As a humanitarian reform to prevent accidents from firedamp, he compelled mine owners to sink two shafts for each coal mine. His most important contribution to chemistry was his spiral periodic arrangement of the elements.

Courtesy Mme. Jean Presne and the *École Supérieure des Mines*, Paris.

Another very early classification of the elements was made by Lewis Reeve Gibbes, professor of chemistry at the College of Charleston, South Carolina, who worked out the first version of his "Synoptical Table of the Chemical Elements" between 1870 and 1874, and in 1875 discussed an improved form of it before the Elliott Society of Charleston. The hardships of the reconstruction period, however, made prompt publication impossible. When the paper was finally published in 1886, it attracted little attention because the periodic tables of Lothar Meyer and Mendeléeff were already well known (*39*).

Instead of arranging all the elements in the order of increasing atomic weights, as the European scientists had attempted to do, Gibbes (probably without knowledge of their work) conceived the idea of assembling the well-known families on horizontal lines numbered from minus four to plus three to correspond with the principal valence of the elements in each family. In each of these horizontal rows, however, he placed the elements in the order of increasing atomic weights. He then found that throughout this table, which he had based on stepwise change of valence, most of the elements in the vertical rows also followed one another in the order of increasing atomic weights. Thus his approach to the problem of classifying the elements was the reverse of that used by Lothar Meyer and Mendeléeff.

Gibbes observed certain blank spaces in his table and recognized the possibility that these might some day be filled by newly discovered elements. He differentiated the two subgroups of each family of elements and recognized the peculiarities of the "typical elements" or "group introducers," carbon, nitrogen, oxygen, and fluorine. He also constructed a spiral chart based on his "Synoptical Table." Although it resembled somewhat the earlier table of Beguyer de Chancourtois, it was doubtless an independent discovery. A much more detailed account of the life and work of Professor Gibbes is to be found in an article by Wendell H. Taylor in the JOURNAL OF CHEMICAL EDUCATION for September, 1941 (*39*).

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XXII. SOME ELEMENTS PREDICTED BY MENDELÉEFF

Three of the undiscovered elements whose properties Mendeléeff foretold in great detail, ekaaluminum, ekaboron, and ekasilicon, were discovered within fifteen years from the time of their prediction. The first was found by Lecoq de Boisbaudran in France, the second by Lars Fredrik Nilson in Sweden, and the third by Clemens Winkler in Germany. These elements were named gallium, scandium, and germanium in honor of these countries.

. . . . . .

> *Die wirklich erfolgreiche Durchführung anorganisch-chemischer Arbeiten ist nur demjenigen möglich, der nicht allein theoretischer Chemiker, sondern auch vollendeter Analytiker ist, und zwar nicht nur ein praktisch angelernter mechanischer Arbeiter, sondern ein denkender, gestaltender Künstler (1).**
>
> *Reinheit der Substanzen ist die Feinheit des Ganzen (6).*†

When Mendeléeff predicted that occupants would be found for the vacant spaces in the periodic system, he little dreamed that three of them would be discovered during his lifetime.

Lecoq de Boisbaudran
1838–1912

French chemist who discovered gallium, samarium, and dysprosium, and perfected methods of separating the rare earths. He ranks with Bunsen, Kirchhoff, and Crookes as one of the founders of the science of spectroscopy.

Gallium

One of these elements, which he called ekaaluminum, was soon revealed by Paul Émile (dit François) Lecoq de Boisbaudran. He was born in Cognac on April 18, 1838, a descendant of the Protestant nobility. His father and brothers were distillers, and Paul Émile also in time became a member of the firm. His mother, a gifted, well-educated woman, taught him foreign languages, the classics, and history. By studying the syllabi of the École Polytechnique, he acquired a splendid scientific foundation, especially in his favorite branches, physics and chemis-

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* The truly successful performance of researches in inorganic chemistry is possible only to one who is not only a theoretical chemist but also an accomplished analyst and, moreover, not merely a practically trained, mechanical worker, but a thinking, creative artist.

† Translated on p. 407.

try. Throughout his life he was encouraged by the sympathy and intelligent aid of his entire family, for, according to Sir William Ramsay, their watchwords were "justice, kindness, and the sense of personal responsibility." An uncle helped him to finance a small private laboratory, and it was there that ekaaluminum, or gallium, was discovered (*2*).

The finding of this element was by no means accidental. Boisbaudran had been studying spectra for fifteen years, and had found that in those emitted by several metals of the same family, the lines are repeated according to the same general arrangement. Anxious to verify this law for the aluminum family, and to find the missing member between aluminum and indium, he reasoned that, since most minerals had already been carefully analyzed, there was little hope of finding new elements among the essential constituents of these minerals. The difficulty of recognizing an unknown element present only as a trace did not escape him, for he said, "The uncertainty which inevitably reigns over the exact chemical reactions of a hypothetical substance, defined only by its position in a natural series, renders quite problematical a success founded solely on the direct application of these reactions *calculated in advance;* for the least error in predicting one of these can throw the substance being sought out of the analytical position which theory assigns to it" (*3*), (*11*).

From Hofmann's "Zur Erinnerung an vorangegangene Freunde"

ADOLPH WURTZ
1817–1884

Professor of chemistry at the École de Médecine in Paris. Discoverer of methyl and ethyl amines and the synthesis of hydrocarbons from alkyl iodides and sodium. He studied the oxidation products of the glycols and the homologs of lactic acid. The proof of the elementary nature of gallium was demonstrated in his laboratory by Lecoq de Boisbaudran.

In February, 1874, Boisbaudran began to investigate some zinc blende from the Pierrefitte mine in the Argeles Valley in the department of Hautes Pyrénées (*11*), (*13*). When he dissolved the ore and placed metallic zinc in the solution, a deposit formed on the zinc. When he heated this deposit with the oxy-hydrogen flame and examined it with the spectroscope, he saw two lines that had never been seen before. These, however, did not appear when he heated the deposit simply with the Bunsen burner.

The following account of the discovery was written by Boisbaudran himself for *Chemical News:*

> Between three and four in the evening of August 27, 1875, I found indications of the probable existence of a new elementary body in the products of the chemical examination of a blende from Pierrefitte. The oxide, or perhaps a sub-salt, is thrown down by metallic zinc in a solution containing chlorides and sulfates. It does not appear to be the metal itself which is reduced by the zinc. . . .
>
> The extremely small quantity of the substance at my disposal did not permit me to isolate the new body from the excess of zinc accompanying. The few drops of zinc chloride in which I concentrated the new substance gave under the action of the electric spark a spectrum composed chiefly of a violet ray, narrow, readily visible, and situate at about 417 on the scale of wave-lengths. I perceived also a very faint ray at 404 (*4*), (*16*).

ÉMILE-CLÉMENT JUNGFLEISCH*
1839–1916

French chemist and pharmacist. Professor of organic chemistry at the École Supérieure de Pharmacie and at the Collège de France. Although most of his ninety-nine papers were organic or pharmaceutical in nature, he also made valuable contributions to the chemistry of gallium and indium.

A month later Boisbaudran performed in Wurtz's laboratory in Paris, in the presence of the chemistry section of the Institute, a series of experiments to prove that gallium, the metal he had discovered and named in honor of France, is a true element. In order that he might attempt to isolate the metal, the technical zinc-mining societies known as "La Vieille Montagne" and "La Nouvelle Montagne" presented him with a quantity of gallium minerals.

Boisbaudran decomposed several hundred kilograms of the crude zinc blende in aqua regia containing excess hydrochloric acid. He also used a slight excess of blende in order that all the nitric acid might be consumed. After filtering off the insoluble matter, he placed sheets of zinc in the acid filtrate in order that the copper, arsenic, lead, cadmium, indium, thallium, mercury, selenium, silver, bismuth, tin, antimony, and gold might be deposited. Before the acid had been entirely consumed by the zinc, Boisbaudran filtered off this spongy deposit. By adding a large excess of zinc to the filtrate, and heating the mixture for several hours on the water bath, he was able to precipitate the basic salts of zinc and the hydroxides of aluminum, iron, gallium, cobalt, and chromium.

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* The portrait of Jungfleisch was obtained through the kindness of Dr. Tenney L. Davis, Massachusetts Institute of Technology.

Although gallium sulfide does not precipitate from a solution of the pure salt, it is readily carried down with zinc sulfide. Boisbaudran therefore added ammonium acetate and acetic acid to the hydrochloric acid solution of the above precipitate, and passed in hydrogen sulfide. As long as the line Ga α (417.0) continued to show in the spectrum of the precipitate, he kept on adding zinc to the filtrate until finally all the gallium had been precipitated.

By dissolving gallium hydroxide in caustic potash, and electrolyzing the solution with a current from five or six Bunsen cells, Boisbaudran prepared more than a gram of gallium metal. This was first prepared in November, 1875. On December 6th he presented 3.4 milligrams of solid gallium (*14*) to the Academy of Sciences, and three months later he presented a specimen of the liquid metal. Since gallium, when free from the solid phase, has a great tendency to remain in the superfused state, this specimen may have remained liquid even at a temperature below 30° Centigrade (*17*). Boisbaudran and Jungfleisch afterward worked up four thousand kilograms of the blende at the Javel works, and obtained seventy-five grams of the metal (*18*).

Properties Predicted for Ekaaluminum (Ea) by Mendeléeff	Properties Found for Boisbaudran's Gallium (Ga)
Atomic weight about 68.	Atomic weight 69.9.*
Metal of specific gravity 5.9; melting point low; non-volatile; unaffected by air; should decompose steam at red heat; should dissolve slowly in acids and alkalies.	*Metal* of specific gravity 5.94; melting point 30.15; non-volatile at moderate temperature; not changed in air; action of steam unknown; dissolves slowly in acids and alkalies.
Oxide: formula Ea_2O_3; specific gravity 5.5; should dissolve in acids to form salts of the type EaX_3. The hydroxide should dissolve in acids and alkalies.	*Oxide:* Ga_2O_3; specific gravity unknown; dissolves in acids, forming salts of the type GaX_3. The hydroxide dissolves in acids and alkalies.
Salts should have tendency to form basic salts; the sulfate should form alums; the sulfide should be precipitated by H_2S or $(NH_4)_2S$. The anhydrous chloride should be more volatile than zinc chloride.	*Salts* readily hydrolyze and form basic salts; alums are known; the sulfide is precipitated by H_2S and by $(NH_4)_2S$ under special conditions. The anhydrous chloride is more volatile than zinc chloride.
The element will probably be discovered by spectroscopic analysis.	Gallium was discovered with the aid of the spectroscope.

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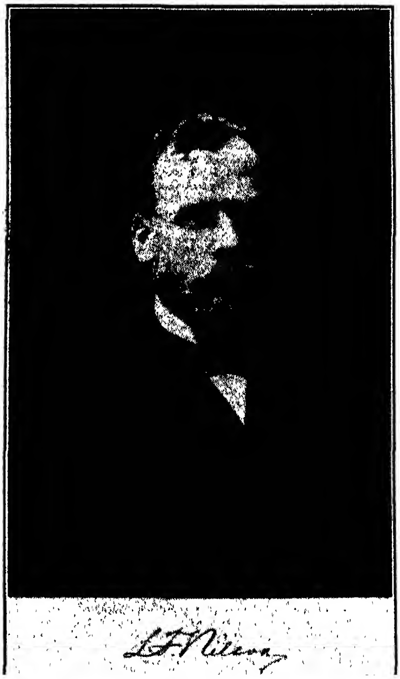
* The 1943 atomic weight of gallium is 69.72.

In discovering this element Lecoq de Boisbaudran was guided, not by the periodic table and the predictions of Mendeléeff but by his own law of spectra (*31*). On November 22, 1875, however, the great Russian chemist stated in the *Comptes rendus* (*15*) that he believed gallium to be identical with ekaaluminum (*20*). Further study of the properties of the new element and its compounds fully confirmed this view (*19*), as is evident from the foregoing table.

Boisbaudran's researches on the rare earths also yielded a rich harvest of results, for he discovered samarium and dysprosium (*2*). His investigations in the field of spectroscopy were also of high merit.

Boisbaudran spoke English fluently, but without regard for fine distinctions, and he sometimes made the mistake of translating his French thoughts too literally. According to Sir William Ramsay, he once startled his dinner partner, a dignified, elderly English lady, with the remark, "The soup is devilish hot." Like Berzelius, he married late in life. His contributions to science were cut short by the pain and disability resulting from severe anchylosis of the joints, but he stoically bore this misfortune for many years until death relieved him on May 28, 1912, at the age of seventy-four years (*2*), (*12*).

Although gallium is one of the rarest of elements, it has an interesting use. Since it melts at about 30° Centigrade and boils at about 1700°, a gallium-in-quartz thermometer can be used for measuring high temperatures far above the range of the ordinary mercury-in-glass thermometer.



From A. G. Ekstrand's Minnesteckning

LARS FREDRIK NILSON
1840–1899

Professor of analytical chemistry at the University of Upsala and at the Agricultural Academy at Stockholm. Discoverer of scandium. His researches on soils and fertilizers transformed the barren plains of his native island into an agricultural region. With Otto Pettersson he investigated the rare earths and prepared metallic titanium.

Scandium

Mendeléeff had predicted that another element, which he called ekaboron and which he said would have an atomic weight between 40 (calcium) and 48 (titanium), would some day be revealed (*20*). It was discovered in 1879 by Lars Fredrik Nilson. He was born on May 27, 1840, in Östergötland, was educated at Visby and at the Linköping Gymnasium, and at the age of nineteen years went to Upsala to study biology, chemistry, and geology.

Just as he was ready to take his examinations for the doctorate in 1865, he received word that his father had been seriously injuried. Although Lars Nilson himself was then in very poor health, and suffering from frequent hemorrhages from the lungs, he immediately returned to Gothland Island, took charge of the farm, purchased an engine and a threshing machine, harvested the crops, and cheered and encouraged his sick father. After a few months, both father and son were in good health. Life in the open air had quickly cured Nilson's lung trouble, and he enjoyed good health for the rest of his life (*5*).

He returned to Upsala, passed his examinations successfully, and was placed in charge of the laboratory. Here, among Berzelius' balances, blowpipes, and preparations, he became a true disciple of that great master. After completing some researches on the compounds of selenium, Nilson and Pettersson began to study the mineral euxenite, hoping to measure the chemical and physical constants of the rare earth elements and their compounds and thus to verify the periodic law. Although they never succeeded in this, Nilson extracted sixty-three grams of the rare earth erbia from gadolinite and euxenite, and converted it into the nitrate. Upon decomposing this salt by heat, as Marignac had done, he obtained some very pure ytterbia and, to his great surprise, an earth that was unknown to him (*21*).

Upon thoroughly investigating this new earth, he found that it contained an element whose properties coincided almost exactly with those Mendeléeff had predicted for ekaboron. Nilson called it *scandium* (*22*) in honor of his fatherland, and it was indeed appropriate that it should be named for the little country where so many new elements had been discovered (*6*). The identity of scandium and Mendeléeff's hypothetical ekaboron was pointed out by Per Theodor Cleve (*20*), (*25*). The table on p. 405 shows the predicted and observed properties of this element (*19*).

BERZELIUS* AT THE AGE OF FORTY-FOUR YEARS

This represents him as he appeared in 1823 when the youthful Friedrich Wöhler came to Stockholm to study chemistry.

The spectra of scandium and ytterbium were first studied by Tobias Robert Thalén (*22*), (*32*). Although scandium salts possess no visible ab-

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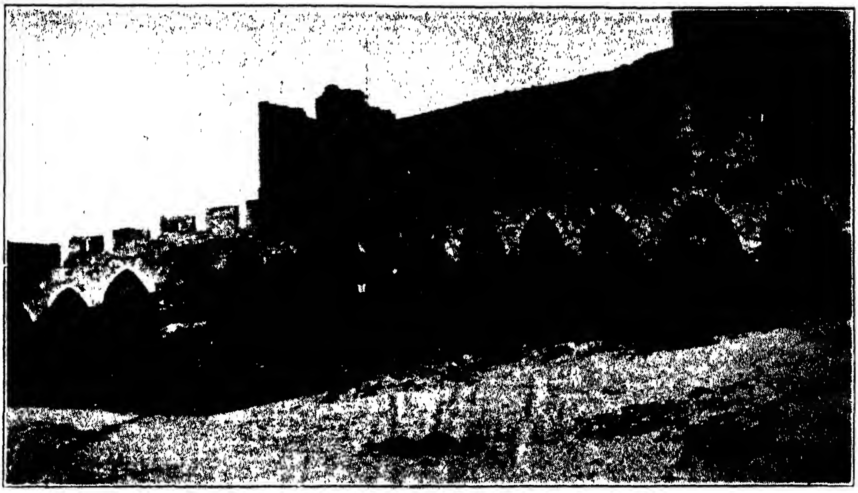
* Reproduced from the late H. G. Söderbaum's "Jac. Berzelius-Levnadsteckning" by kind permission of the author.



INSIDE THE CITY WALL OF VISBY[*]

Lars Fredrik Nilson, the discoverer of scandium, received his early education in this beautiful old city on Gothland Island.

PROPERTIES PREDICTED FOR EKABORON (Eb) BY MENDELÉEFF	PROPERTIES FOUND FOR NILSON'S SCANDIUM (Sc)
Atomic weight 44.	Atomic weight 44.[†]
It will form one oxide Eb_2O_3 of specific gravity 3.5; more basic than alumina, less basic than yttria or magnesia; not soluble in alkalies; it is doubtful if it will decompose ammonium chloride.	Scandium oxide, Sc_2O_3, has a specific gravity of 3.86; is more basic than alumina, less basic than yttria or magnesia. It is not soluble in alkalies and does not decompose ammonium chloride.
The salts will be colorless and give gelatinous precipitates with potassium hydroxide and sodium carbonate. The salts will not crystallize well.	Scandium salts are colorless, and give gelatinous precipitates with potassium hydroxide and sodium carbonate. The sulfate crystallizes with difficulty.
The carbonate will be insoluble in water; and probably precipitated as a basic salt.	Scandium carbonate is insoluble in water, and readily loses carbon dioxide.
The double alkali sulfates will probably not be alums.	The double alkali sulfates are not alums.
The anhydrous chloride, $EbCl_3$, should be less volatile than aluminum chloride, and its aqueous solution should hydrolyze more readily than that of magnesium chloride.	Scandium chloride, $ScCl_3$, begins to sublime at 850°. Aluminum chloride begins to sublime above 100°. In aqueous solution the salt is hydrolyzed.
Ekaboron will probably not be discovered spectroscopically.	Scandium was not recognized by spectrum analysis.

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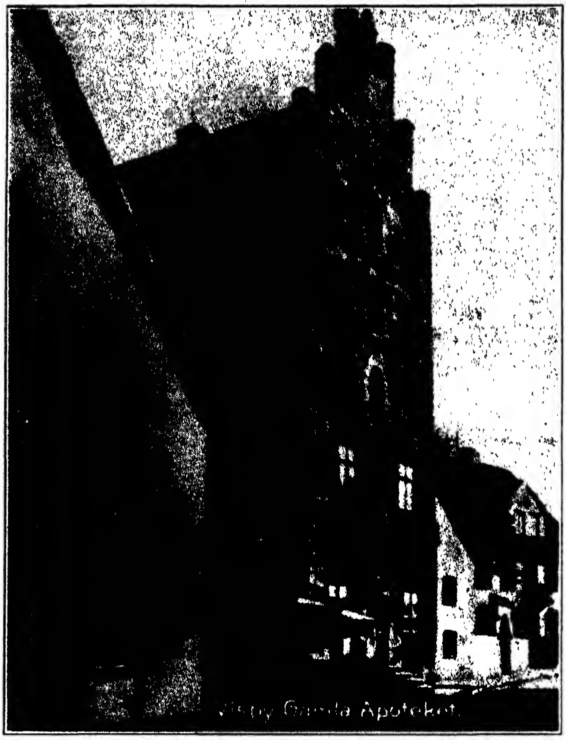
[*] Photo by Miss Mary Larson, Dept. of Zoölogy, The University of Kansas.

[†] The 1943 atomic weight of scandium is 45.10.

sorption spectrum, the element may be detected by means of spark and arc spectra (*24*), (*33*). The atomic weights of both these elements were soon determined by Nilson (*23*).



OLD APOTHECARY SHOP AT VISBY*

From 1878 to 1883 Nilson served as professor of analytical chemistry at the University of Upsala, but in his later years he taught at the Agricultural Academy at Stockholm. He found that the sterility of the calcareous moors of his native island was caused by lack of potash. After liberal use of kainite fertilizer, recommended by Nilson, Gothland Island began to yield good crops of sugar beets (*6*).

Nilson's long hours in the laboratory left him little time for recreation, but his brief periods of relaxation were free from worry. Otto Pettersson, professor of chemistry at the University of Stockholm, once said of him:

> Whilst it was customary, in the private laboratory where Nilson presided, to enliven the hours of work with conversation, anecdotes, puns, occasionally by a song, etc., it was considered unfitting to introduce scientific matters into the conversation of leisure hours. Nilson positively did not admit it, and woe to him who dared to speak of political or philosophical matters when Nilson intended to be merry. And he was always merry when he was with his friends, the merriest of them all. He had a thousand devices for putting a stop to a conversation which threatened to take a tiresome turn. He would, for example, sit listening for a while with a grave face, and then interpose with a short nonsensical observation, delivered with great solemnity in the accents of some political or scientific worthy of pedantic fame, while a gleam of fun shot forth from under his heavy, dusky eyebrows. The effect was irresistibly comic, so much the more as it came un-

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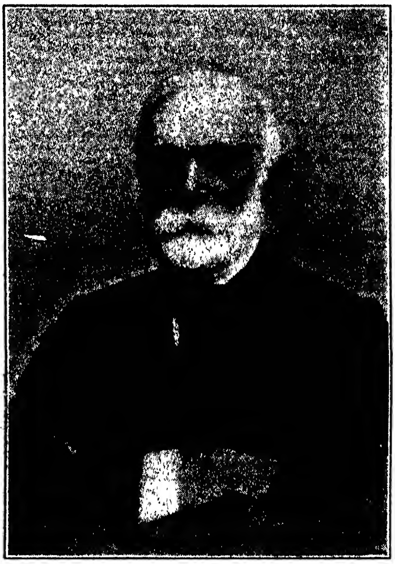
* Photo loaned by Miss Mary Larson, Dept. of Zoölogy, The University of Kansas.

foreseen. His hearers were at first puzzled, then one chuckled, another laughed, and in a minute the impending political or philosophical discourse was drowned in a chorus of laughter in which Nilson's voice at last joined in accents swelling like big waves and rollers of an ocean of mirth (*5*).

Like all successful analysts, Nilson had a passion for neatness and order, and his motto, "*On the purity of substances depends the perfection of the whole,*" is well worth remembering (*6*). He died on May 14, 1899, at the age of fifty-nine years (*34*).



From Hasselberg's, "Biografier. T. R. Thalén"
TOBIAS ROBERT THALÉN
1827-1905

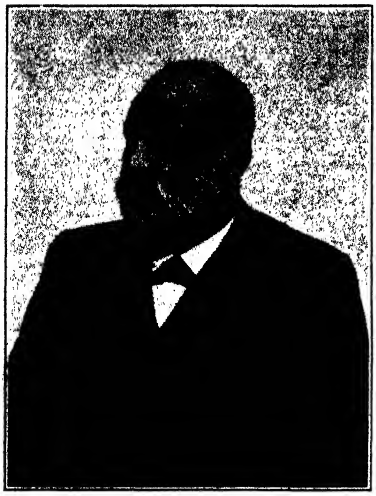
Swedish physicist, astronomer, and spectroscopist. He mapped the spectra of yttrium, erbium, didymium, lanthanum, scandium, thulium, and ytterbium, and in 1866 wrote a historical review of spectrum analysis. He also studied the magnetic properties of iron and iron ores.

Germanium

A third element that Mendeléeff had predicted was to be a member of the silicon family (*20*). This "ekasilicon" was discovered in 1886 by Clemens Winkler, who named it *germanium* in honor of his fatherland. Thus the three "nationalist" elements—gallium in France, scandium in Sweden, and germanium in Germany—were all discovered within fifteen years after their prediction by the great Russian chemist. Although Mendeléeff was the first person to describe the properties of ekasilicon, the gap in the periodic table had been observed about seven years before by the English chemist, Newlands, who had noticed that silicon and tin form the extremities of a triad, the middle member of which was missing (*29*).

Clemens Alexander Winkler was born at Freiberg on December 26, 1838, but grew up in Zschopenthal, a village in the Saxon Erzgebirge where his father, Kurt Alexander Winkler, operated a smalt works. Kurt Winkler was himself a well-known chemist and metallurgist, who had studied under Berzelius and Sefström, and had fitted up an excellent metallurgical laboratory in the smalt works (*7*), (*30*).

Since the son soon learned to love Nature, his father taught him to identify and classify plants, animals, and minerals. The boy, however, never acquired a passion for collecting. He wanted to learn as much as possible about each specimen, but had no desire to own it. At the age of twelve



CLEMENS ALEXANDER WINKLER*
1838–1904

Professor of chemistry at the Freiberg School of Mines. Pioneer in the analysis of gases. Manufacturer of nickel and cobalt. He discovered the element germanium and made pioneer researches on indium.

years he entered the Freiberg gymnasium, where he studied mineralogy under August Breithaupt. Winkler did not like foreign languages, but nevertheless acquired such a thorough mastery of his mother tongue that his scientific papers are valued not only for their genuine scientific merit but also for their beautiful, faultless German (7).

He continued his education at the Realschule, or scientific school, at Dresden and at the Gewerbeschule, or technical school, in Chemnitz, spending the vacations in his father's laboratory. When he entered the Freiberg School of Mines in 1857, he already knew more analytical chemistry than was taught there, and because of this thorough preparation and his sound constitution, he was able to make remarkable progress in research without missing any of the dances and gay parties so dear to a student's heart (7).

His paper on the reactions that take place in the Gay-Lussac towers of sulfuric acid plants resulted from his successful experiments on the absorption of obnoxious sulfur dioxide fumes from an ultramarine plant. In order to analyze the gases, he invented the Winkler gas buret with a three-way stopcock, and perfected his own methods. In the meantime he made his living by producing nickel and cobalt on a commercial scale.

In 1873 he accepted a position as professor of chemical technology and analytical chemistry at Freiberg. G.

PORTRAIT MEDALLION OF BERZELIUS BY DAVID D'ANGERS, 1835†

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* This photograph of Winkler was made by Dr. O. Brunck, Rector of the Freiberg School of Mines, who graciously sent Dr. Dains a copy.

† Reproduced from the late H. G. Söderbaum's "Jac. Berzelius-Levnadsteckning" by kind permission of the author.

D. Hinrichs once said, "The perfection of the analytical work of Winkler astonished me till I found the name of his father, Kurt Winkler, in the list of special students of Berzelius" (*8*). Winkler, who had learned neatness from his father, soon transformed the slovenly laboratories, and trained his students to work so carefully that rubber aprons were not needed. One day, when a new student appeared, wearing a large apron, Winkler exclaimed, "And so you're going to mix lime" (*7*).

NILS GABRIEL SEFSTRÖM*
1787–1845

Director of the School of Mines at Fahlun, Sweden. Discoverer of the element vanadium, which was later shown to be identical with del Río's "erythronium." For a brief biographical sketch of Sefström, see Part XI, pp. 194–98.

In the fall of 1885 there was found, at the approach of a vein in the Himmelsfürst mine near Freiberg, a new ore which the discoverer, Albin Weisbach, a professor of mineralogy at the Freiberg School of Mines, named argyrodite (*28*). Hieronymus Theodor Richter, the chemist who with Ferdinand Reich had discovered indium, made a qualitative blowpipe analysis of the argyrodite, and found that it contained silver, sulfur, and a trace of mercury (*27*). Professor Weisbach then asked Winkler to make a thorough quantitative analysis in order to establish the composition of the mineral. Winkler's results were consistent, but, since they invariably came out 7 per cent too low, he concluded that the ore must contain an unknown element† (*26*).

Believing that the mineral must be a sulfo salt of silver and that the new element must belong in the same analytical group with arsenic, antimony, and tin, he fused a pulverized portion with sodium carbonate and sulfur, took up the melt with water, and filtered off the residue. By making the filtrate *slightly* acidic with hydrochloric acid, he precipitated and removed the sulfides of arsenic and antimony. Now, since the new element had not been removed with any of the precipitates, it would *have* to be present in the filtrate as a sodium sulfo salt. Yet when Winkler added a little more hydrochloric acid, a precipitate containing free sulfur, but no

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* Reproduced from the late H. G. Söderbaum's "Jac. Berzelius-Levnadsteckning" by kind permission of the author.

† The reader will recall that similar results obtained in the analysis of petalite led Arfwedson to the discovery of lithium in 1818. See pp. 278–82, 287–9.

sulfide, was thrown down. Even upon evaporating the filtrate to dryness, he obtained nothing but sodium chloride.

Unwilling to submit to this failure, Winkler toiled incessantly for four months, thinking constantly of the elusive element. On February 6, 1886, he filtered off the precipitated sulfur as he had done so many times before and, reckless with discouragement, poured into the clear filtrate a *large quantity* of hydrochloric acid. To his great delight a heavy, flaky, white precipitate immediately appeared (*9*). This substance, the sulfide of the new element, dissolved readily in ammonium hydroxide, and precipitated again upon addition of a large excess of hydrochloric acid, for it has a most surprising property: it is quite insoluble in concentrated acids, yet readily soluble in water and dilute acids (*7*).

From Goldschmidt's "Erinnerungsblätter an Albin Weisbach"

ALBIN WEISBACH
1833–1901

German mineralogist, crystallographer, and physicist. Discoverer of argyrodite, the mineral in which Clemens Winkler afterward discovered germanium. He was a son of Julius Weisbach, the distinguished mining engineer, and a student of Ferdinand Reich, the discoverer of indium.

The new element, which he called *germanium*, was isolated by heating the dry sulfide in a current of hydrogen. The gray, metallic powder was found to be less volatile than antimony, but the volatility of the chloride explains why Winkler obtained nothing but sodium chloride when he evaporated the filtrate from the precipitated sulfur. The germanium chloride had all been lost as vapor. The ore argyrodite is now known to be a double sulfide of silver and germanium, $GeS_2 \cdot 4Ag_2S$.

Winkler thought at first that germanium was a metalloid like antimony and arsenic, and that it would be found to be identical with Mendeléeff's predicted ekastibium, an element which ought to lie between antimony and bismuth. The scientific world immediately became interested in the new element. On February 26th Mendeléeff contributed to the *Berichte der deutschen chemischen Gesellschaft* a list of properties which the new element would have to have in order to fit into the space between antimony and bismuth. He thought it more likely, however, because of the solubility of the chloride in water and because of the white color of the sulfide, that germanium was ekacadmium, an element between cadmium and mercury. At the same time Victor von Richter of Breslau wrote to Winkler saying he believed germanium to be ekasilicon, the lowest homolog of tin, an undiscovered element between gallium and arsenic. Two days later Lothar Meyer said in the *Berichte* that he, too, believed germanium to be the longed-for ekasilicon, and that he had already expressed that opinion to his advanced students (7).

Winkler's months of discouragement were ended, and he worked joyously, stimulated by the interest and encouragement of these eminent chemists. A vast amount of work remained to be done, and the obtaining of sufficient quantities of germanium compounds became increasingly difficult. Pure argyrodite contains only 7 per cent of germanium, the rich ore had been exhausted, and Winkler was obliged to work up large quantities of the low-grade ore. He had at first hoped to strike richer deposits of argyrodite, and had therefore been too generous with his valuable germanium compounds. Nevertheless, he finally obtained convincing proof that germanium is the ekasilicon predicted by Mendeléeff in 1871. In the following table the predicted properties of ekasilicon are compared with the actual properties of germanium:

	Ekasilicon (Es)	*Germanium* (Ge)
Atomic weight	72	72.32*
Specific gravity	5.5	5.47
Atomic volume	13	13.22
Valence	4	4
Specific heat	0.073	0.076
Specific gravity of dioxide	4.7	4.703
Molecular volume of dioxide	22	22.16
Boiling point of tetrachloride	under 100°	86°
Specific gravity of tetrachloride	1.9	1.887
Molecular volume of tetrachloride	113	113.35

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* The 1947 atomic weight of germanium is 72.60.

Mendeléeff had made only one mistake in his prophecy. He had thought that ekasilicon, like titanium, would be difficult to liquefy and volatilize. Lothar Meyer, who had disagreed with him on this point, proved to be correct. Winkler afterward said that germanium contradicted all expectations in its occurrence in nature. He said that he might have expected to find it combined with oxygen and accompanied by titanium and zirconium in rare Scandinavian minerals, but would never have thought to look for it in silver mines among the related compounds of arsenic and antimony (*10*).

Clemens Winkler made brilliant contributions both to pure and applied chemistry, and had many interests beyond the chemical field Like Davy and Ekeberg, he had poetic ability, and many of his songs are preserved in the songbook of the Freiberg Academy. O. Brunck says that these were written in good form and with well-chosen words (*7*). For the entertainment of his guests, Winkler often used to write humorous chemical verses for them to sing while he played a gay accompaniment on almost any instrument they might prefer. He resigned his professorship in 1902, and died of carcinoma on October 8, 1904. His name will always be honored wherever true scientific greatness is appreciated.

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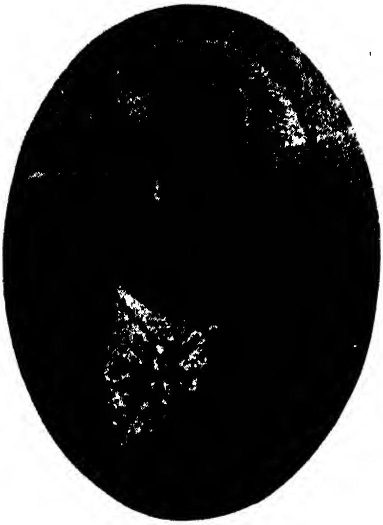
XXIII. THE RARE-EARTH ELEMENTS

The rare earths are so very much alike and occur closely associated in such very complex minerals that it is extremely difficult to separate them. They have all been obtained, however, by elaborate and laborious fractionation of two mixtures, the "yttria" of Gadolin and the "ceria" of Klaproth, Berzelius, and Hisinger, originally believed by their discoverers to be pure oxides. The patient researches of Mosander, Delafontaine, Marignac, Cleve, Boisbaudran, Urbain, Charles James, and many others finally resulted in the decomposition of the so-called "yttria" into the oxides now known as yttria, terbia, erbia, ytterbia, lutecia, holmia, thulia, and dysprosia. Through the persistent skilful work of Mosander, Marignac, Boisbaudran, Brauner, Auer von Welsbach, Demarçay, Hopkins, McCoy, and others, the old "ceria" has finally been broken down into the oxides ceria, lanthana, neodymia, praseodymia, samaria, gadolinia, europia, and illinia. Some of the rare earth elements have only recently been isolated, and most of them are extremely rare and costly even in the form of their compounds.*

. . . .

The rare earths perplex us in our researches, baffle us in our speculations, and haunt us in our very dreams. They stretch like an unknown sea before us, mocking, mystifying, and murmuring strange revelations and possibilities (1).



Johan Gadolin
1760–1852
Professor of chemistry at the University of Åbo, Finland. Discoverer of the complex earth "yttria," which afterward yielded an entire series of simple oxides. He made a thorough study of the rare earth minerals from Ytterby, Sweden.

Rich stores of the rare-earth minerals lay hidden for centuries in the Scandinavian peninsula until, one day in 1788, Lieutenant Arrhenius found an unusual black rock at Ytterby, a little town near Stockholm (*22*), (*69*). The rare earths were afterward discovered in this new mineral by the famous Finnish scientist, Johan Gadolin.

He was born at Åbo near Helsingfors (Helsinki) on June 5, 1760. His father, Jacob Gadolin, a well-known astronomer and physicist, taught him to love and understand Nature. After completing his course at the Uni-

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* The discovery of illinium will be discussed in Chapter XXVII, pp. 524–8.

Courtesy E. R. Schierz

The Gadolin Medal

The Gadolin Fund was established in 1935 by the Society of Finnish Chemists. The first award of this handsome medal was made in 1937 to Ossian Aschan and Gust. Komppa. The obverse bears a portrait of Johan Gadolin, discoverer of gadolinite; the reverse side shows a group of chemists investigating the rare earths from this mineral. *See* ref. (*64*) This picture of the plaster cast of the medal, taken in the studio of the designer, Emil Wikström, was sent to Dr. Schierz by Dr. E. S. Tomula of Helsinki.

Åbo, Finland, in 1823

Johan Gadolin, the discoverer of the first rare earths, was born in Åbo, and served there for twenty-five years as professor of chemistry.

versity of Åbo, he studied under Bergman at Upsala, and acquired a broad education through travel in Denmark, Germany, Holland, and England (*43*). In 1794 Gadolin investigated the mineral Lieutenant Arrhenius had found at Ytterby, and found that it contained about 38 per cent of a new earth. Ekeberg soon confirmed the analysis (*40*), (*41*), and mineralogists afterward named the mineral *gadolinite* in honor of the Finnish chemist (*64*).

Gadolin served the University of Åbo as a professor of chemistry for twenty-five years (1797–1822), and during this time he made a thorough study of the wonderful Ytterby minerals. He also studied fluxes for decomposing iron ores for analytical purposes, made contributions to thermochemistry, helped solve the questions of chemical proportions and chemical affinity, and published the first Swedish textbook that embraced Lavoisier's views (*43*).

CARL GUSTAV MOSANDER*
1797–1858

Swedish army surgeon, chemist, and mineralogist. Curator of the mineral collections at the Stockholm Academy of Sciences. Professor of chemistry and mineralogy at the Caroline Institute. Discoverer of lanthana and didymia. The latter earth was afterward split by Auer von Welsbach into praseodymia and neodymia.

He lived for thirty years after his retirement, and died at Wirmo, Finland, on August 15, 1852, at the age of ninety-two years (*65*). In 1827 the city of Åbo and the university buildings were destroyed by fire, and Gadolin's valuable mineral collections were lost. The University was then transferred to Helsingfors (*2*).

Yttria and Ceria

Ekeberg (*40*), (*41*), Klaproth, and Vauquelin all investigated Gadolin's new oxide, and it came to be called *yttria*, a name derived from Ytterby. In 1803 Klaproth discovered in the mineral cerite another earth which he called "*terre ochroite*," but which is now known as *ceria*.† Berzelius and Hisinger also discovered ceria independently, but upon further investigation neither their yttria nor their ceria proved to be a pure oxide (*3*).

Lanthana and Didymia

The proof of the complexity of ceria and yttria was given by Carl Gustav

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* Reproduced from H. G. Söderbaum's "Jac. Berzelius. Levnadsteckning" by kind permission of the late Dr. Söderbaum.

† See Chapter XVIII, pp.322–5

Mosander, one of Berzelius' assistants. He was born at Kalmar on September 10, 1797, was educated as a pharmacist and physician, and served for some time as an army surgeon (*4*). For many years he lived in the same house with Berzelius, and his wife, who was of Dutch ancestry, helped Berzelius to acquire a reading knowledge of that language (*5*). When the Stockholm Academy of Sciences moved into its magnificent new "palace," as Berzelius called it, Mosander became curator of the mineral collections, and was given an apartment adjoining them. He also had charge of the chemical laboratory for medical students at the Caroline Institute, where he served as professor of chemistry and mineralogy for many years.

He and Wöhler often used to go on long tramps together during the latter's memorable months at Stockholm, and Mosander helped his German friend prepare a valuable mineral collection to take back to his fatherland. Berzelius' letters to Wöhler contain frequent references to Mosander under the affectionate nickname "Pater Moses." On October 12, 1824, for example, Berzelius wrote:

Courtesy of the late M. Elizabeth Farson

CARL AXEL ARRHENIUS
1757–1824

Swedish chemist and mineralogist. In 1788 he discovered in the Ytterby quarry a new black rock which he named *ytterbite*. In 1794 Gadolin discovered the complex earth "yttria" in this mineral, which has since been renamed *gadolinite*.

> Now here I am alone, chemically deserted. Pater Moses is now working for his examination, Hisinger has not yet returned, and Arfvedson, who was recently engaged, is moored near his fiancée. . . However, my time is spent as usual in a certain pleasant monotony and in moving back and forth between the writing desk and the laboratory, where I am still busy with trifles, for example with the completion of the works begun on the preparation of lithia, yttria, and zirconia. . . .

In November of the same year he wrote again:

> A thousand, thousand thanks for the interesting letter and for the beautiful minerals, which I arranged in their proper places several days ago. Father Moses thanks you no less than do I. I cannot accustom myself to the thought of no longer finding Wöhler at his desk in the laboratory, and even though I prefer to see Moses' face there rather than none at all, yet the loss by the deception is too great. . . .

It may be assumed that Mosander passed his examinations successfully, for on July 15, 1825, Wöhler wrote to his Swedish master, "Moses heisst wohl jetzt Hr. Doctor Pater Moses, wozu ich gratulire"*(*6*).

In 1839 Mosander heated some cerium nitrate and treated the partly decomposed salt with dilute nitric acid. In the extract he found a new earth, which he named *lanthana*, meaning *hidden*, meanwhile retaining the old name, *ceria*, for the oxide which is insoluble in dilute nitric acid (*7*), (*28*), (*45*). In the same year, Axel Erdmann, one of Sefström's students, discovered lanthana in a new Norwegian mineral, which he named *mosandrite* in honor of Mosander.

On February 1st Berzelius wrote to Wöhler:

JOHAN AUGUST ARFWEDSON†
1792–1841

Metallurgist, chemist, and mineralogist. The discoverer of lithium. He studied the action of hydrogen on metallic sulfates, and in 1823, by heating the green oxide of uranium in a current of hydrogen, he prepared uranous oxide, UO_2, which he believed to be the metal. He studied under Berzelius. (The spelling *Arfvedson* appears frequently in the literature.) See pp. 285–94.

> It is completely confirmed. When I showed Erdmann's little specimen to Mosander, he announced that he, too, had found something new in cerite. Although we see each other every day, he had never breathed a word of it to me. . . . I do not think that during the month when I was ill, Mosander did any work on his earth. I almost surmise that he thought, "Let Berzelius worry about it; I shall then be free from a lot of drudgery." A few days ago he began again. At first he let it be understood that what Hisinger and I had called cerium was a mixture of two oxides, neither of which possessed the properties of the mixture. . . . I have now studied pure ceric oxide and found that addition of the earth does not change any of its properties. If this were not the case, the dis-

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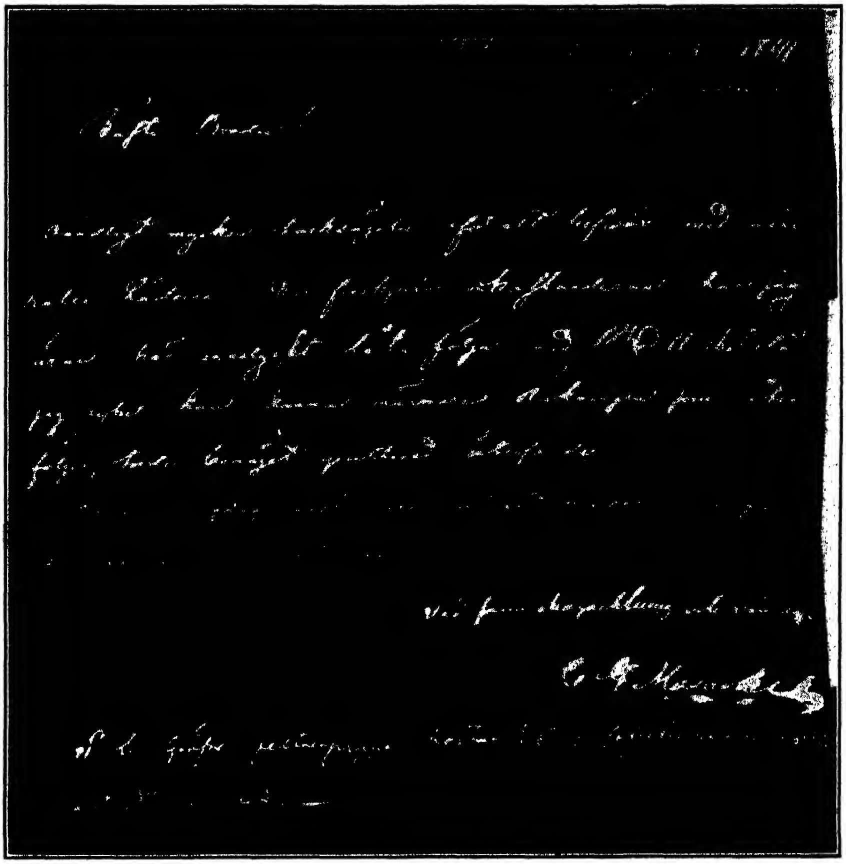
* "Moses may now be called Herr Doctor Father Moses, wherefore I offer congratulations."

† Reproduced from H. G. Söderbaum's "Jac. Berzelius. Levnadsteckning" by kind permission of the late Dr. Söderbaum.



Edgar Fahs Smith Memorial Collection,
University of Pennsylvania

AUTOGRAPH LETTER OF C. G. MOSANDER

His script is almost illegible, but the following is an approximate translation:* "Stockholm, Nov. 5, 1841. Dear Brother: Especially great thanks to you for all your trouble with my specimens. The expense I have the honor to include is . . (amount illegible), as nearly as I can estimate it. The account is enclosed. Would you please receipt it? Once again many thanks to you for all your trouble. Many greetings to Westring. . Respectfully and cordially, C. G. Mosander. P. S. Coarse filter paper costs . . ."

> covery of the earth would have occurred before Mosander. . . . . Mosander would not tell me what he expects to name his new earth. The communications I am now making are for you alone. You must not publish anything about them. . . .

On February 12 he wrote, "Mosander seems willing to take my sug-

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* The writer is deeply grateful to Miss Mary Larson of the Zoölogy Department at The University of Kansas and to Mr. Einar Bourman for the translation of this letter from the Swedish and for assistance in securing Swedish illustrations.

gestion to name it (the element) *lanthanum* (*lanthan*) and the oxide, *lanthanum oxide* or *lanthana* (*lanthanerde*)" (*8*).

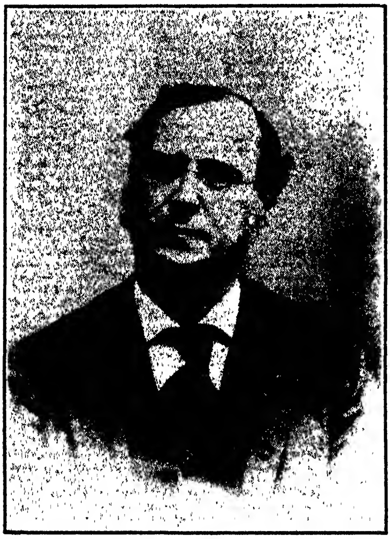
Months passed by, and on June 18th Berzelius wrote again to Wöhler:

> I can give you no news from Mosander. For a long time he has not worked at the continuation of his experiments, and he no longer makes any mention of what he is finding, not so much from reserve as because he is not doing anything; but he has his mineral-water establishment to manage, so that he really has very little time. . . . If you write to Mosander yourself, you will probably receive something from him for the *Annalen.*

Courtesy Central Scientific Co.

DIDYMIUM GLASS GOGGLES

A special glass containing didymium is now used to protect the eyes of the glass blower. It transmits all light except the yellow glare from the hot sodium glass. See "Goggles for precision glass blowing," J. CHEM. EDUC., 9, 214 (Feb., 1932).



Courtesy Miss Elizabeth Farson and Mr. Jules Delafontaine

MARC DELAFONTAINE

1837–1911

Swiss chemist who studied under J.-C.-G. de Marignac and taught for a time at the University of Geneva. Arriving in New York in 1870, he followed the advice of Louis Agassiz and went to teach in the High Schools of Chicago. He also served as analytical chemist and expert for the Chicago Police Department in famous criminal cases, and carried on research in spectrum analysis.

Wöhler waited patiently for several months, and then wrote on February 25, 1840, "The chemical world cannot understand why Mosander has not yet published anything on lanthanum." Two years later Berzelius wrote, "Mosander still keeps working at his lanthanum, but says very little about it. Meanwhile I have learned enough to know that more depends on it than had been supposed."

On May 13, 1842, Berzelius again broached the subject to Mosander. To use his own words:

> I suggested to Father Moses that we soon have a paper on cerium for the *Annalen.* He laughed rather scornfully, went down into his laboratory, for he lives in the house of the Academy, and brought up a mortar half full of a white,

> slightly yellowish powder, and asked, "What is that?" I admitted my ignorance. "That, Sir," he said, "is the way ceric oxide looks when one has it pure. It has cost me a year's work to get that far." He added that he was not going to publish any of his results until he had them completely finished. Although he comes up nearly every morning to chat with me a while, and usually complains about the difficulties which keep him from getting pure preparations, he tells me nothing about his real results, and I am satisfied, for it will be all the more interesting when one gets them all at once (*9*).

In 1841 Mosander had treated lanthana with dilute nitric acid, and had extracted from it a new rose-colored oxide, which he believed contained a new element. He named the new metal *didymium* because, as he said, it seemed to be "an inseparable twin brother of lanthanum" (*27*), (*29*), (*46*).

Wöhler objected to this name because *Didym*, the German form of it sounds rather childish and silly, "etwas Kindisches, etwas Läppisches." Berzelius replied in Mosander's defense:

> No, my dear friend, I have no liking for this name, and yet I do not want to, and cannot, ask Mosander to change it, since he has announced it publicly. You surely do not understand our friend Father Moses. He takes suggestions from no one. The proposal to change a name given by him would be an offense which he would not easily pardon, and still he would not change it. He intentionally looked for a name beginning with *D* in order to have a symbol unlike those for other metals. To be sure, it is quite true, as you say, that the repetition of the same consonants, and of almost the same vowel sounds, has an unpleasant sound; but one soon gets accustomed to it, and finds it endurable, and you must do the same.

JEAN-CHARLES GALISSARD DE MARIGNAC, 1817–1894

Swiss chemist who discovered ytterbia and gadolinia and made many important contributions to the chemistry of the rare earths. Professor of chemistry at the University of Geneva. He made precise determinations of the atomic weights of many elements, and, by separating tantalic and columbic acids, proved that tantalum and columbium (niobium) are not identical.

Berzelius then mentioned a number of accepted organic names which sound much worse than "Didym" (*10*). Didymia was regarded as a pure earth until 1885, when the late Auer von Welsbach decomposed it.

Yttria, Erbia, and Terbia

Having shown that the earth originally called *ceria* was composed of an insoluble portion, *ceria*, and a soluble portion, *lanthana*, Mosander investigated yttria in a similar manner (*7*). In 1843 he showed that yttria from which all the ceria, lanthana, and didymia have been removed contains at least three other earths. These are: a colorless oxide, for which he kept the name *yttria;* a yellow earth, *erbia;* and a rose-colored one, *terbia.* He separated them by fractional precipitation with ammonium hydroxide. Erbia, the least basic of the three, separated in the first fractions, while yttria, the most basic one, was found in the last fractions (*23*).

Edgar Fahs Smith Memorial Collection, University of Pennsylvania

J. LAWRENCE SMITH
1818–1883

American mineralogical and analytical chemist. His method of decomposing ores which are to be analyzed for sodium and potassium is still the standard procedure. He investigated the rare earths in samarskite and verified Mosander's conclusions regarding the complex nature of yttria.

Mosander's work was confirmed by Delafontaine, Marignac, J. Lawrence Smith, Cleve, and Boisbaudran, but, for some reason, a confusing shift of names occurred. The names *erbia* and *terbia* were interchanged, so that the former now applies to the rose-colored oxide (*3*). The names of the four elements, *yttrium*, *ytterbium*, *erbium*, and *terbium*, have all been derived, by the way, from that of the little Swedish town, Ytterby, where the rare earth minerals were first found.

Before closing this brief account of Mosander's work, it seems fitting to reflect for a moment over his sincere tribute to his honored teacher. On April 18, 1848, he wrote regarding a translation of Berzelius' textbook:

> My dear Wöhler: In this case as always, I follow the irresistible impulse of my heart to say openly what I believe to be right; you may once more test it, and then judge, and I am convinced that you will appreciate the truth of what I have to say. The great master will perhaps soon pass into another world, but by us and our successors his name will long be honored and loved, and what he has accomplished here—that you know as well as I do—was not done for the sake of vainglory, but out of pure zeal for truth and enlightenment, and the motive for his researches has always sprung from a pure source; then shall the right of defending Science and himself, ere his life is extinguished, be denied him in the last moment when he could devote

his undiminishedmental powers to the service of Science? Impossible. .... Literal translation or none (*11*).

Berzelius died at Stockholm on August 7, 1848. His mind remained clear until the end, but during the last six days he lay half asleep, and spoke no more. Mosander died ten years later, on October 15, 1858, at Ångsholm near Drottningholm (*4*).

Erbia, Ytterbia, and Scandia

In 1878 the Swiss chemist Marignac discovered that erbia contained a new earth which he called *ytterbia* (*21*). Jean-Charles Galissard de Marignac, a descendant of a Huguenot family that had fled from Languedoc early in the eighteenth century, was born in Geneva on April 24, 1817. When he was sixteen years old, he entered the École Polytechnique at Paris. He also spent two profitable years at the School of Mines, and then rounded off his education by traveling through Scandinavia and Germany. In 1840 he went to Giessen to study under Liebig, but, in spite of the latter's influence, he preferred inorganic chemistry to organic.

PORTRAIT OF BERZELIUS FROM A DAGUERREOTYPE TAKEN IN BERLIN IN 1845, THREE YEARS BEFORE HIS DEATH*

BETTY BERZELIUS NÉE POPPIUS (BARONESS BERZELIUS),* 1811-1884

Daughter of state councilor, G. Poppius. When she married Berzelius in 1835 he was already a man of great renown, and the baronetcy was conferred on him at the wedding. See Chapter IX, p. 167.

Marignac's life work, which, like that of Stas, consisted in making many precise determinations of atomic weights in order to test Prout's hypothesis, won Berzelius' sincerest praise, for he wrote:

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* Reproduced from H. G. Söderbaum's "Jac. Berzelius. Levnadsteckning" by kind permission of the late Dr. Söderbaum.

> I place the highest value on your experiments concerning atomic weights. The patience with which you repeat each experiment a large number of times, the sagacity with which you vary your methods, making use only of those which can give reliable results, and the conscientious manner in which you give the numbers dictated by the balance ought to assure for you the complete confidence of chemists (*44*).

After working for a time at the Sèvres porcelain works, Marignac returned to Switzerland to accept a modest position as professor of chemistry at the Geneva Academy. From 1845 to 1878 he taught both chemistry and mineralogy, and carried on his researches in a damp, dark cellar. During the last ten years of his life, he lay prostrate, suffering intensely from a disease of the heart, from which death finally brought release on April 15, 1894 (*12*).

P. T. CLEVE
1840–1905
Swedish chemist, geologist, botanist, and hydrographer. Professor of chemistry at Upsala. Discoverer of thulium and independent discoverer of holmium.

He began his study of the rare earths in 1840, when he was barely twenty-three years old. According to P. T. Cleve, "Marignac's work on the rare earths is undoubtedly the most important in this particular department of chemistry" (*13*). In 1878 Marignac heated some erbium nitrate from gadolinite until it decomposed. When he extracted the resulting mass with water, he obtained two oxides: a red one, for which he retained the name *erbia*, and a colorless one, which he named *ytterbia* (*13*), (*42*), (*57*). In the following year Nilson isolated the earth *scandia*,* the oxide of Mendeléeff's predicted eka-boron, from ytterbia.

Erbia, Holmia, and Thulia

The erbia left after the removal of ytterbia and scandia was still further resolved by Per Theodor Cleve,† who was born on February 10, 1840. He was the thirteenth child of a Stockholm merchant. After graduating from the University of Upsala in 1863, he studied for a time in Wurtz's laboratory in Paris, and in 1874 he became a professor at Upsala. True lover of Nature that he was, he could never confine his activities closely to

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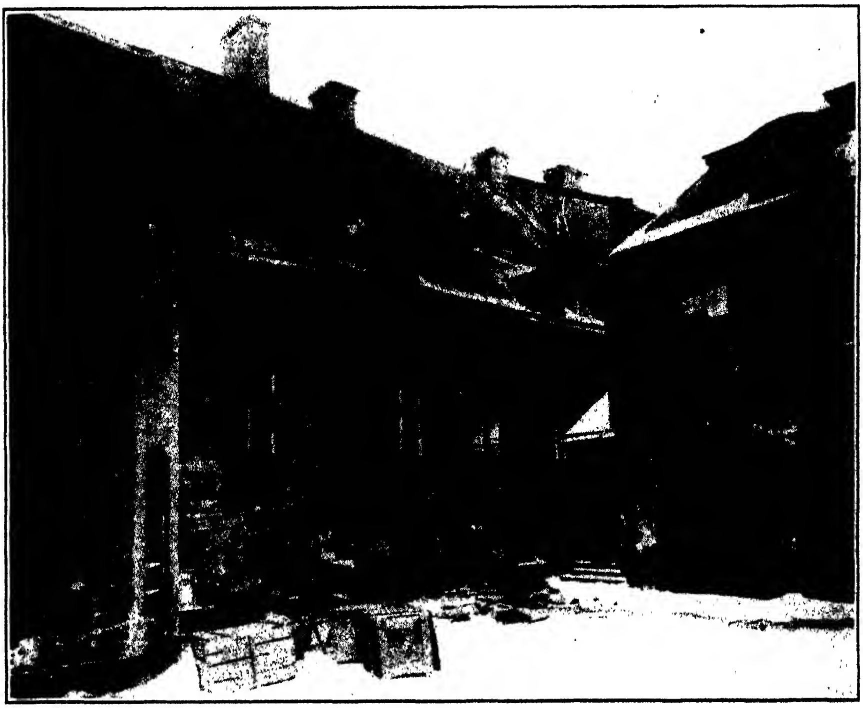
* See Chapter XXII, pp. 403–7.

† For additional biographical notes on Cleve, see J. CHEM. EDUC., 7, 2698 (Nov., 1930).

one branch of science, but was interested alike in chemistry, geology, botany, and hydrography. He wrote his scientific papers in a lucid, pleasing style, and also produced literature of esthetic value (*14*).

Cleve's fame rests chiefly, however, on his discoveries among the rare earths. After obtaining some erbia from which all the ytterbia and scandia had been removed, and after noticing that the atomic weight of the erbium was not constant, he succeeded in resolving the earth into three constituents: *erbia*, *holmia*, and *thulia* (*21*). The absorption bands of holmium had already been noticed by the Swiss chemists M. Delafontaine and J.-L. Soret (1827–90), who had announced the existence of an "element X," later found to be identical with Cleve's holmium (*35*). Since Cleve was an independent discoverer of the element holmium, his name for it has been accepted by chemists (*14*), (*36*), (*67*). Holmium was named for Cleve's native city, and the word *thulium* is derived from *Thule*, an old name for Scandinavia.



INTERIOR COURT OF A GERMAN BAKER'S HOUSE. BERZELIUS' LABORATORY AT THE RIGHT*

* Reproduced from H. G. Söderbaum's "Jac. Berzelius. Levnadsteckning" by kind permission of the late Dr. Söderbaum.

PORTRAIT OF JÖNS JACOB BERZELIUS*
1779–1848
FROM A PAINTING BY J. WAY
Berzelius was an independent discoverer of the earth "ceria" and much of the early research on the rare earths was done in his laboratory.

In spite of his devotion to organic and inorganic chemistry, Cleve never lost interest in biology. During his later years he made an extended study of the plankton of Skagerak and the North Sea, especially of the fresh-water algae and diatoms, in order to locate the ocean currents.

Although he found little time to mingle with his colleagues, he enjoyed an occasional happy, social evening with his family and friends. Hans and Astrid Euler said of him, "His merry irony played upon all those for whom unyielding principles and passionateness caused unnecessary trouble, and upon scientific pedantry no less than upon religious and social prejudice; he himself was liberal in the broadest sense of the word, and unyielding only in his rectitude." He retired from teaching at the age of sixty-five years, hoping to devote the rest of his life to the study of plankton. He died a few months later, however, on June 18, 1905, after severe suffering with pleuritis (*14*).

BARON AUER VON WELSBACH
1858–1929
Austrian chemist and chemical technologist. Discoverer of praseodymium and neodymium. Inventor of the Welsbach gas mantle, the osmium filament electric lamp, and the automatic gas lighter.

Samaria and Gadolinia

Marignac believed as early as 1853 that Mosander's didymia was not a pure substance, and later spectroscopic work of Delafontaine and of Boisbaudran indicated that the spec-

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* Reproduced from H. G. Söderbaum's "Jac. Berzelius: Levnadsteckning" by kind permission of the late Dr. Söderbaum.

trum of didymia varied according to its source. Boisbaudran in 1879 added ammonium hydroxide to a solution of it, and noticed that another earth precipitated before the didymia. Since the spectrum of this new oxide was found to be different from that of didymia, Boisbaudran concluded that it must be a new earth, which he named *samaria* (*26*), (*27*). In 1886 he obtained from it still another earth, which, however, proved to be identical with the substance which Marignac had separated from samarskite in 1880, and to which he had given the provisional name Y_α (*3*). With Marignac's assent, Boisbaudran named this oxide *gadolinia* (*34*), (*57*). Both these earths were named for minerals in which they occur, samarskite and gadolinite.

A RECONSTRUCTION OF BERZELIUS' BIRTHPLACE AT WÄFVERSUNDA (VÄVERSUNDA), SWEDEN, SHOWING THE BUILDINGS AS THEY APPEARED IN HIS TIME*

Neodymia and Praseodymia

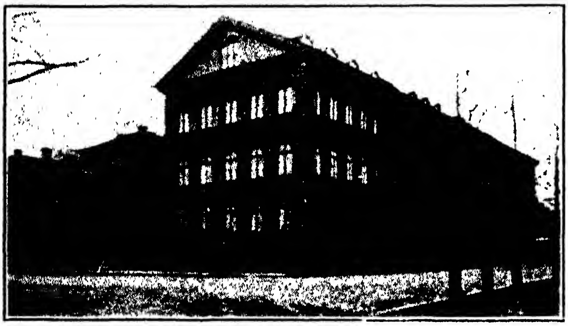
Marignac, Lecoq de Boisbaudran, Cleve, and Bohuslav Brauner all believed didymium to be a mixture of elements, but none of them were able to make the difficult separation (*49*). In 1882 the late Professor Brauner of the University of Prague examined some of his didymia fractions with the spectroscope and found a group of absorption bands in the blue region (λ = 449–443) and another in the yellow one (λ = 590–568) (*53*), (*66*).†

* Reproduced from H. G. Söderbaum's "Jac. Berzelius. Levnadsteckning" by kind permission of the late Dr. Söderbaum.

† See p. 565.

These two groups of bands are now known to belong to two earths, *praseodymia* and *neodymia*, respectively, which the late Baron Auer von Welsbach obtained in 1885 by splitting didymia (*3*), (*30*), (*32*), (*58*).

Carl Auer, Baron von Welsbach, was born on September 1, 1858, at Vienna (*4*). After completing the courses at the gymnasium and Polytechnicum of his native city, he went to Heidelberg to study under Bunsen. The quiet, industrious, unsociable boy from Austria soon became a favorite of the great German master. Auer was deeply interested in inorganic chemistry, and especially in minerals. The rare earth minerals of the north attracted him so much that he began to search for specimens. Although the first little collection that he showed to Bunsen would not have filled a child's hand, Bunsen laughingly told him to begin his investigation (*16*) Carl Auer's researches on the rare earths, which were begun in this modest manner at Heidelberg, were continued for the rest of his life.



THE CAROLINE INSTITUTE OF MEDICINE AND SURGERY AT STOCKHOLM. BOTH BERZELIUS AND MOSANDER TAUGHT CHEMISTRY AT THIS SCHOOL OF MEDICINE

On June 18, 1885, he announced to the Vienna Academy of Sciences that by repeated fractionation of ammonium didymium nitrate he had succeeded in splitting didymia into two earths, for which he proposed the names *praseodymia* and *neodymia*, *green didymia* and *new didymia*. Many chemists were skeptical, and he afterward said, "Only Bunsen, to whom I first showed the discovery, recognized immediately that a splitting of didymium had actually been accomplished. This acknowledgment from Bunsen, who had, as is known, published very beautiful and comprehensive researches on didymium, showed how unselfishly this great investigator used to judge the researches of younger men" (*16*). Neodymia and praseodymia have never been decomposed into simpler oxides.

Baron Auer is best remembered for his invention of the incandescent gas mantle, a truly great advance in the history of illumination (*55*). Instead of attempting to produce a gas which would burn with a luminous flame, he decided to use a non-luminous flame to heat a refractory mantle to incandescence. The problem, as he said, "was not to find a process by which an infusible compound could be given a definite shape. This invention is founded, above all, on the fact, proved by numerous experiments, that molecular mixtures of certain oxides are possessed of properties which cannot be deduced from those of their constituents." One of the engineers to whom he explained his plans said, "In my works we only take notice of serious ideas."

After many discouragements Baron von Welsbach finally impregnated the fabric for the mantles in a mixture containing one thousand grams of thorium nitrate, ten grams of cerium nitrate, five grams of beryllium nitrate, 1.5 grams of magnesium nitrate, and two thousand grams of water (*15*). His first patent for the incandescent lamp, known in Germany as the "Auerlicht" and in America as the *Welsbach mantle*, was dated September 23, 1885.

Baron Auer chose as his motto the appropriate words "*more light*," but preferred to write it "*plus lucis*" as a reminder of his early struggles with Latin (*49*). In 1901 Kaiser Franz Josef elevated him to the hereditary nobility with the title of Freiherr von Welsbach. When the Kaiser remarked, "You have had, so I hear, considerable success with your discoveries," Baron von Welsbach quickly replied, "Yes, Your Majesty, up to the present more than 40,000 people throughout the entire world have found employment through my discoveries." This reply left Franz Josef speechless (*16*).

Auer von Welsbach also invented the automatic gas lighter based on a pyrophoric alloy of iron and cerium, and the osmium-filament electric lamp (*54*), the first successful electric-light bulb with a metallic filament, which, however, was soon superseded by the tungsten and tantalum lamps.

(*Courtesy Dr. Ethel M. Terry (Mrs. H. N. McCoy*)

HERBERT NEWBY McCOY, 1870-1945

American chemist who has made outstanding contributions to radioactivity and the chemistry of the rare earths. In 1904 he showed that radium is produced by spontaneous transmutation of uranium. Three years later, in collaboration with W. H. Ross, he pointed out the identical chemical behavior of the compounds of certain elements which F. Soddy later called *isotopes*. Dr. McCoy also gave the first quantitative proof that the α-ray activity of uranium compounds is directly proportional to their uranium content.

His home, Welsbach Castle, commanded a glorious view of the Carinthian Alps, and his chief recreations were hunting, fishing, and gardening. In the park were many exotic plants, including cedars from Lebanon, that he had carefully nurtured until they could withstand the severe climatic conditions at the high altitude of 800 meters. On the ground floor of the castle there was a well-equipped laboratory containing a valuable spectroscope which his aunt had provided for his early researches, a library of valuable books with uncut pages, which had belonged to Bunsen, and an unsurpassed collection of rare earths. These treasures were carefully guarded by the ever-faithful "Buzi," a terrier who allowed no one but his master to touch even a piece of paper. On August 2, 1929, Baron Auer was seized with severe abdominal pain. After a painful examination by physicians, who realized the serious nature of the illness, "he got up, went into the garden, looked around, closed up his study, burned a few papers, stood for a long time before his father's portrait, then went into the laboratory, covered his spectroscope, stroked it tenderly with his hand, glanced at the other things, took leave of his last unfinished thulium series with a motion of the hand, closed the rooms again, and quietly lay down" (*49*). Twelve hours later he entered into eternal rest.


EUGÈNE-ANATOLE DEMARÇAY
1852–1904

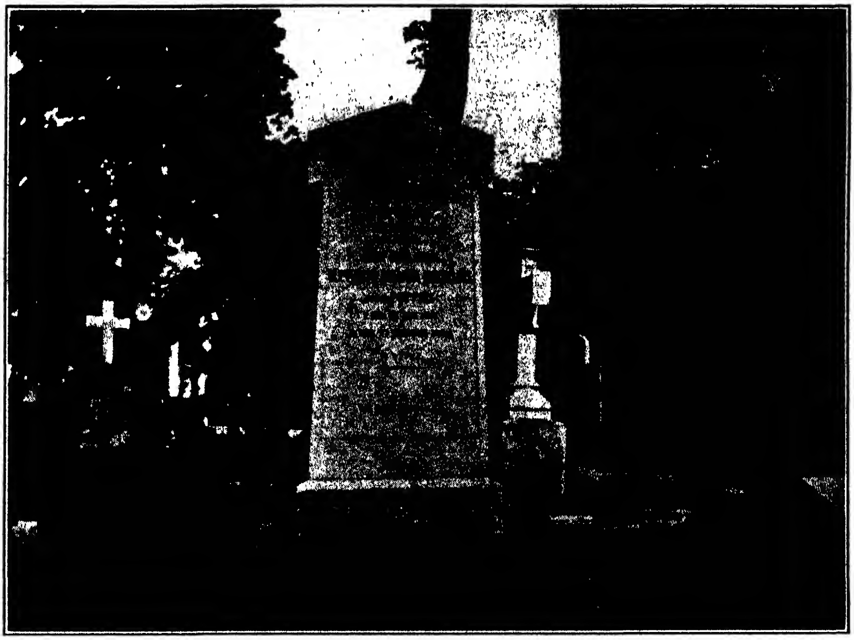
French chemist who discovered the element europium and gave spectroscopic proof of the discovery of radium by M. and Mme. Curie. He investigated many terpenes and ethers, and studied the volatility of metals at low temperatures and pressures.

Holmia and Dysprosia

In the year 1886 Lecoq de Boisbaudran separated pure holmia into two earths, which he called *holmia* and *dysprosia*. He accomplished this by fractional precipitation, first with ammonium hydroxide and then with a saturated solution of potassium sulfate, and found that the constituents of impure holmium solutions precipitate in the following order: terbium, dysprosium, holmium, and erbium (*3*), (*37*), (*48*). Lecop de Boisbaudran never had an abundant supply of raw materials for his remarkable researches on the rare earths, and he once confided to Professor Urbain that most of his fractionations had been carried out on the marble slab of his fireplace (*56*).

Samaria and Europia

Eugène-Anatole Demarçay, the discoverer of europium, was born in Paris on New Year's Day, 1852. He studied at the Lycée Condorcet, spent a year in England, and at the age of eighteen years entered the École Polytechnique (*4*). He was interested not only in chemistry, but also in geology, natural history, and languages. His good humor, intellectual integrity, and ability to think independently soon won the respect and friendship of his professors, Cahours, Wurtz, Deville, Dumas, Friedel, Cornu, Schützenberger, and Lecoq de Boisbaudran, and his love of pure science brought him into contact with many younger investigators, including Moissan, Becquerel, and the Curies. After serving for some time as Cahour's assistant at the École Polytechnique, he gave up his position in order to travel through Algeria, Egypt, and India (*50*). When he returned to Paris, he devoted all his time to research in pure science.



BERZELIUS' GRAVE* IN THE SOLNA CHURCHYARD

His first investigations, begun in 1876, were in organic chemistry. His study of the C_5 terpenes and the ethers of the unsaturated acids proved to be of practical value in the perfume industry. While studying the sulfides of nitrogen he suffered a serious accident. The explosion of a cast-iron vessel completely destroyed one of his eyes, yet, after recovering from the injury and shock, he continued his dangerous researches on compressed gases. In his famous laboratory on the Boulevard Berthier he had the finest apparatus for producing vacua to be found in Paris. This was used for studying the volatility of zinc, cadmium, and gold at low temperatures and pressures (*50*).

* Reproduced from H. G. Söderbaum's "Jac. Berzelius. Levnadsteckning" by courtesy of the late Dr. Söderbaum.

In order to study the effect of very high temperatures on spark spectra, Demarçay constructed an induction coil with a short secondary wire of large diameter, which gave intensely hot, luminous, globular sparks. By using electrodes of very pure platinum, he was able to eliminate from the spectrum of the substance he wished to examine all foreign spectra except the well-known lines of platinum. This was the apparatus with which he studied the spectra of the rare earths.

In 1901 Demarçay made an elaborate series of fractionations of samarium magnesium nitrate which resulted in the discovery of a new earth, ***europia*** (*3*), (*31*), (*59*). Since he could read a complex spectrum "like an open book," he was frequently called upon to pass judgment on supposedly new elements, and was the first to observe the new lines of radium in some barium salts brought by Pierre Curie.

Had he been granted a longer life, Demarçay might have made a more thorough study of the compounds of europium, but in 1904 death brought an end to his researches. Although he had realized for some time that his life would soon be cut short, he nevertheless felt "grateful for the years he had lived" and "asked for no further reward than that felt by a keen intelligence when it gives rise to a flash of thought that will be remembered throughout the world" (*50*).

Courtesy Dr. R. E. Oesper

GEORGES URBAIN, 1872-1938

French chemist, painter, sculptor, and musician. President of the Société de Chimie and of the International Committee on Atomic Weights. His enthusiasm for research was acquired from Pierre Curie and Charles Friedel. *See* ref. (*70*).

Ytterbia and Lutecia

In 1907 Georges Urbain separated ytterbia into two constituents. By repeated fractional crystallization of ytterbium nitrate from nitric acid solution, he obtained two oxides with different properties. One of these he named ***neoytterbia*** in order, as he said, "to leave to the illustrious Marignac, in the future, the credit of his fundamental discovery" (*52*). The other oxide he called ***lutecia*** from an old name for his native city, Paris (*3*), (*38*), (*39*), (*51*). The element he named ***neoytterbium*** is now known simply as ***ytterbium***. Although these elements were found to be identical with the "aldebaranium" and "cassiopeium" discovered independently by Auer von Welsbach at about the same time, Urbain's names for them have been widely accepted.*

Georges Urbain was born on April 12, 1872, received his doctorate from the University of Paris in 1899, and afterward became a professor there (*4*). He received inspiration and encouragement in his researches from Pierre Curie and Lecoq de Boisbaudran (*53*). Until his death on November 5, 1938, he was a professor at the Sorbonne and chief of the chemical division of the French Institute of Physico-Chemical Biology founded by Baron Edmond de Rothschild (*17*). Professor Urbain was a member of the Institute of France and of the International Commission on Atomic Weights. He is famous not only for his work on the rare earths (*52*), spectroscopy, magnetism, cathode phosphorescence, and atomic weights, but also for his beautiful artistic productions, among which may be mentioned the plaque which he designed in honor of the Schützenberger centennial (*18*), (*70*).

Courtesy Tenney L. Davis

MEMORIAL PLAQUE DESIGNED BY GEORGES URBAIN IN HONOR OF THE SCHÜTZENBERGER CENTENNIAL. THIS IS A FINE EXAMPLE OF PROFESSOR URBAIN'S ARTISTIC ABILITY.

Before the news of Urbain's discovery reached America, the late Professor Charles James of the University of New Hampshire had prepared a large amount of very pure lutecia. Although deeply disappointed because his caution and delay in publishing his results had caused him to lose priority

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* In German periodicals, however, lutecium is called cassiopeium.

in this discovery, he accepted Urbain's results without question and never pushed his own claim (*19*), (*60*).

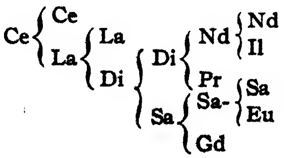
Charles James was born at Earls Barton, near Northampton, England, on April 27, 1880. At the age of nineteen years he entered University College, London, where Sir William Ramsay and his colleagues had recently discovered the inert gases. From 1906 until his untimely death in 1928, Professor James served as an inspiring teacher of chemistry at the University of New Hampshire. He published in the *Journal of the American Chemical Society* about sixty papers on the rare earth elements, worked out processes for extracting them from their minerals and separating them one from another, made accurate determinations of their atomic weights, and discovered new rare earth compounds. He often prepared these substances in unusually large amounts and generously shared them with other investigators (*60*).

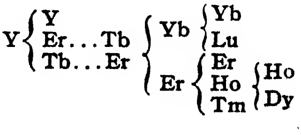
Professor James displayed remarkable ingenuity in devising new, economical, and efficient methods of separating the rare earths and in observing the progress of these separations by photographing the spectra of his products. After thorough study of the solubilities of the rare earth bromates, he worked out a bromate method of fractionating the members of the cerium group. The James method of fractional crystallization of the double magnesium rare earth nitrates is probably the most widely used means of separating this group into fractions (*60*).

Although it is extremely difficult to prepare rare earth salts pure enough for atomic weight determinations, the James values for thulium, samarium, and yttrium agree almost exactly with the atomic weights accepted by the International Committee. Professor James also made outstanding contributions to the chemistry of other rare elements such as scandium, gallium, germanium, beryllium, and uranium (*60*).

This remarkable work was all accomplished during a very short span of life. Professor James died in Boston on December 10, 1928 at the age of forty-eight years. In the following year, a fine, new, four-story chemistry building at the University of New Hampshire was named in his honor (*19*).

The following diagrams which Professor James prepared for the Fourteenth Edition of the Encyclopedia Britannica show very clearly the separations by which the original complex earths "ceria" and "yttria" were resolved into the simple oxides of the rare earth metals.





The metals of the rare earths comprise the largest of all the natural groups (*25*), (*47*). All of them except holmium and illinium have been prepared in the metallic state (*20*), (*24*), (*33*), (*61*), (*62*), (*63*), (*68*).

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XXIV. THE HALOGEN FAMILY

The discovery of the four halogens required a little more than a century. Although Scheele prepared chlorine in 1774 by the action of manganese dioxide on hydrochloric acid, it was believed to be a compound until after 1810, when Sir Humphry Davy gave convincing proof of its elementary nature. In 1811 Bernard Courtois isolated iodine from the mother liquor obtained by leaching the ashes of marine algae. Balard's discovery of bromine fifteen years later was an especially important event in the history of science, for chemists were just beginning to realize that there are family groups among the elements and Döbereiner soon observed that chlorine, bromine, and iodine form a closely related triad. The long, dangerous search for fluorine, which brought suffering and death to several promising chemists, culminated successfully in 1886 through the brilliant efforts of Moissan.

. . . . . .

> *La recherche d'un corps simple est toujours très captivante (1), (17).**
>
> *La science ne paraît pas seulement avoir pour mission de satisfaire chez l'homme ce besoin de tout connaître, de tout apprendre, qui caractérise la plus noble de nos facultés; elle en a aussi une autre, moins brillante sans doute, mais peut-être plus morale, je dirai presque plus sainte, qui consiste à coördonner les forces de la nature pour augmenter la production et rapprocher les hommes de l'égalité par l'universalité du bien-être (2).†*

Chlorine

In his famous research on pyrolusite, Scheele allowed hydrochloric acid, or *spiritus salis* as he called it, to stand in contact with finely ground pyrolusite (crude manganese dioxide), and noticed that the acid acquired thereby a suffocating odor like that of warm aqua regia, and "most oppressive to the lungs." He thought that the manganese dioxide had taken the combustible principle, phlogiston, from the hydrochloric acid, and therefore called the gas *"dephlogisticated marine acid,"* or *"dephlogisticated muriatic acid."* He noticed that it dissolved slightly in water, imparting to it an acid taste, that it bleached colored flowers and green leaves, and that it attacked all metals (*3*).

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* The search for an element is always captivating.

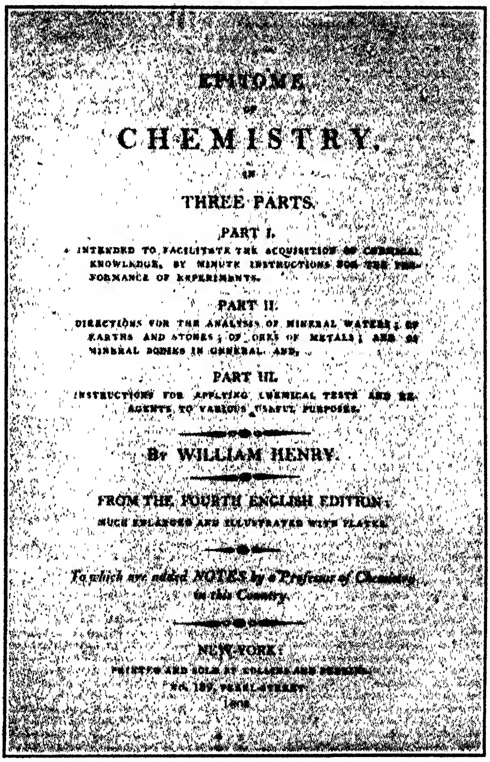
† Science appears to have as its mission not merely the satisfaction of man's need of learning and understanding everything, which characterizes the noblest of our faculties; it has another aim, doubtless less brilliant but perhaps more moral, I would almost say more sacred, which consists in coördinating the forces of nature to increase production and make men more nearly equal by the universality of comfort.

Lavoisier thought that all acids contain oxygen. Dr. William Henry, who obtained hydrogen by passing an electric discharge through gaseous "marine acid," concluded that it came from the water, and that water must be an essential constituent of hydrochloric acid (*37*), (*38*). Berthollet, who was a partisan of Lavoisier and not a phlogistonist, noticed that calcined pyrolusite, which had lost some of the oxygen from its manganese dioxide, yielded less of the suffocating gas, "dephlogisticated marine acid," than could be obtained from an equal weight of fresh pyrolusite. He concluded that:

WILLIAM HENRY, 1775–1836

British chemist and manufacturer, and author of books on chemistry. He discovered that when a gas is absorbed in a liquid, the weight dissolved is proportional to the pressure of the gas (Henry's law). He thought that water was an essential constituent of hydrochloric acid.

> It is therefore to the vital air [oxygen] of the manganese [pyrolusite], which combines with the marine acid, that the formation of the dephlogisticated marine acid is due. I ought to state that this theory was presented and announced some time ago by M. Lavoisier, and that M. de Fourcroy made use of it in his "Elements of Chemistry and Natural History" to explain the properties of dephlogisticated marine acid such as they were then known.



EPITOME
OF
CHEMISTRY,
IN
THREE PARTS.

PART I.
INTENDED TO FACILITATE THE ACQUISITION OF CHEMICAL KNOWLEDGE, BY MINUTE INSTRUCTIONS FOR THE PERFORMANCE OF EXPERIMENTS.

PART II.
DIRECTIONS FOR THE ANALYSIS OF MINERAL WATERS; OF EARTHS AND STONES; OF ORES OF METALS; AND OF MINERAL BODIES IN GENERAL. AND,

PART III.
INSTRUCTIONS FOR APPLYING CHEMICAL TESTS AND REAGENTS, TO VARIOUS USEFUL PURPOSES.

BY WILLIAM HENRY.

FROM THE FOURTH ENGLISH EDITION;
MUCH ENLARGED AND ILLUSTRATED WITH PLATES.

To which are added NOTES by a Professor of Chemistry in this Country.

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TITLE PAGE OF WILLIAM HENRY'S "EPITOME OF CHEMISTRY"

In the original, Benjamin Silliman's autograph can be seen just above the words "Professor of Chemistry."

Berthollet thought that the gas now known as chlorine was a loose compound of hydrochloric acid and oxygen, or, to use his own words, that:

> [Dephlogisticated marine acid] is manifestly formed by the combination of vital air with marine acids but in it the vital air is deprived of a part of the principle of elasticity, and adheres so feebly to the marine acids that the action of light suffices to disengage it promptly, light having more affinity for its base than marine acid has (*4*).

In the year 1807 Sir Humphry Davy obtained hydrogen by the action of potassium on "muriatic acid," and concluded that it must have come from the water in the acid, and that the oxygen in the water must have converted the potassium to potassium oxide (*5*). Gay-Lussac and Thenard, however, did not accept this explanation. They argued that the hydrogen came neither from the acid nor from the water, but from the potassium, which was thereupon changed back into caustic potash, which then reacted with the acid. They tested the "oxidized marine acid" (chlorine) with glowing charcoal, but, since they could detect no oxygen, they concluded that oxygen was formed only in the presence of water. All their attempts to decompose the chlorine by heating it with dry charcoal proved fruitless (*6*).

COUNT CLAUDE-LOUIS BERTHOLLET
1748–1822

French chemist and physician. Professor at the Ecole Normale. He collaborated with Lavoisier in his researches and in reforming chemical nomenclature. Berthollet's "Essai de statique chimique" emphasized the importance of the relative masses of the reacting substances in chemical reactions.

SIR HUMPHRY DAVY
1778–1829

British chemist who isolated the alkali and alkaline earth metals and boron, and proved that chlorine is an element. Gay-Lussac and Thenard isolated boron independently at about the same time.

Gay-Lussac and Thenard believed (1) that muriatic gas contains one-fourth of its weight of water, (2) that oxymuriatic gas is a compound of oxygen and some other substance, and (3) that the substance obtained by heating calomel with phosphorus is a triple compound consisting of dry muriatic acid, oxygen, and phosphorus. Davy's final views on these three points were as follows: (1) muriatic acid is composed of oxymuriatic acid (*chlorine*) and hydrogen, (2) chlorine is an element, and (3) the substance obtained by heating calomel with phosphorus is a compound of the elements chlorine and phosphorus (*7*).

Since Berthollet, Gay-Lussac, Thenard, Fourcroy, and Chaptal all belonged to the French school founded by the illustrious Lavoisier, it was difficult for them to admit the existence of an acid that contained no oxygen, but nevertheless they soon had to yield to the convincing evidence presented by Sir Humphry (*8*), (*41*). Dr. John Murray in Edinburgh and Berzelius in Stockholm continued, however, for some time to regard chlorine as a compound.

JÖNS JACOB BERZELIUS,* 1779–1848

He was one of the last chemical authorities to be convinced of the elementary nature of chlorine.

After iodine was discovered in 1811, the evidence for the elementary nature of chlorine became still more convincing, and by 1820 even Berzelius had yielded (*9*). When Anna, his cook, remarked one day that the flask she was washing smelled of "oxidized muriatic acid," Berzelius replied, "Anna, you mustn't speak of oxidized muriatic acid any more; from now on you must say chlorine" (*10*).

The discovery of bromine by Balard and the preparation of prussic (hydrocyanic) acid, an oxygen-free acid, by Gay-Lussac made the evidence conclusive. Davy's formal announcement of the elementary nature of chlorine was made in a memoir which he read before the Royal Society on November 15, 1810 (*8*).

Sir Humphry Davy's life was a short one, and his last years were marred by continued illness. In a letter written in Rome in February, 1829, he

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* Reproduced from H. G. Söderbaum's "Jac. Berzelius Levnadsteckning" by kind permission of the late Dr. Söderbaum.

said, "If I die, I hope that I have done my duty and that my life has not been vain and useless" (*50*). Three weeks later he was stricken with palsy, from which he never recovered. Even the devotion and medical skill of his younger brother, Dr. John Davy, were in vain. When spring came, Dr. Davy thought it best to take his brother from Rome to Geneva in order to avoid the hot Italian summer. The long journey by horse and carriage was most exhausting, and Sir Humphry died at Geneva on May 29, 1829. His desire that his life might be useful was so richly fulfilled that his name will always be honored as that of a supremely great scientist and humanitarian.

ANNA SUNDSTRÖM,[*] BERZELIUS' HOUSEKEEPER

She kept house for him for many years before he was married and prepared the meals in the kitchen-laboratory, where his sand bath on the stove was never allowed to cool. Berzelius once said that he could not have thus entrusted the management of his home to any other person of the servant class.

Iodine[†]

Iodine, one of the most beautiful of all the elements, was first observed in 1811 by Bernard Courtois, who was born on February 8, 1777, in a house just across the street from the famous old Dijon Academy. His father, Jean-Baptiste Courtois, was a saltpeter manufacturer who used to assist Guyton-Morveau, the lawyer, in his brilliant lectures on chemistry. Thus the son lived constantly in a chemical environment, dividing his time between the paternal saltpeter works and the laboratories of the Academy.

After Citizen Guyton was called to the Legislative Assembly in 1791, J.-B. Courtois gave up his position at the Academy in order to devote all his time to the manufacture of niter. After assisting his father for a time, Bernard was apprenticed for three years to a pharmacist at Auxerre, M. Fremy, the grandfather of Edmond Fremy, the famous chemist. In

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[*] Reproduced from H. G. Söderbaum's "Jac. Berzelius. Levnadsteckning" by kind permission of the late Dr. Söderbaum.

[†] The pictures of the Dijon Academy, the sealed tube containing the first iodine, and the Courtois autograph letter have been reproduced by courtesy of Dr. L. G. Toraude from his book, "Bernard Courtois et la Découverte de l'Iode." The autograph letter belongs to the departmental archives of the Côte d'Or. The photograph of the sealed tube was taken at Dijon on Nov. 9, 1913, the day of the ceremony in honor of the one hundredth anniversary of the discovery of iodine.

the meantime Guyton-Morveau had become the director of the École Polytechnique, and through his intervention Bernard Courtois was admitted to the laboratories of this school to study under Fourcroy. Here he entered into his research and courses in pure chemistry with pleasure and enthusiasm. In 1799, however, he was called to serve his country as a pharmacist in the military hospitals. In 1804, while serving as *préparateur* under Armand Seguin, he made an important investigation of opium (*51*).

Although J.-B. Courtois failed in business, he was an honest man, and both father and son struggled hard to pay their creditors. In 1808 Bernard Courtois married Madeleine Eulalie Morand, a young girl of humble parentage who could barely read and write.

From Toraude's "Bernard Courtois et la Découverte de l'Iode"

THE OLD DIJON ACADEMY (B) AND THE BIRTHPLACE (E) OF BERNARD COURTOIS (PRESENT CONDITION OF THE BUILDINGS)

In the middle of the nineteenth century the latter building was enlarged and made higher. The street at C is the Rue Monge (formerly *Rue du Pont Arnauld*). When it was widened, the quarters in the Academy Building formerly occupied by Bernard's father, Jean-Baptiste Courtois, assistant to Guyton-Morveau, were torn down.

Along the coasts of Normandy and Brittany many plants live at shallow depth in the ocean, and some of them are cast ashore by the waves and tides. For plants such as these the French writers of the early nineteenth century used the term *varech*,* from which the English words *wrack* and *wreck* have been derived (*13*). By burning *Fucus*, *Laminaria*, and other

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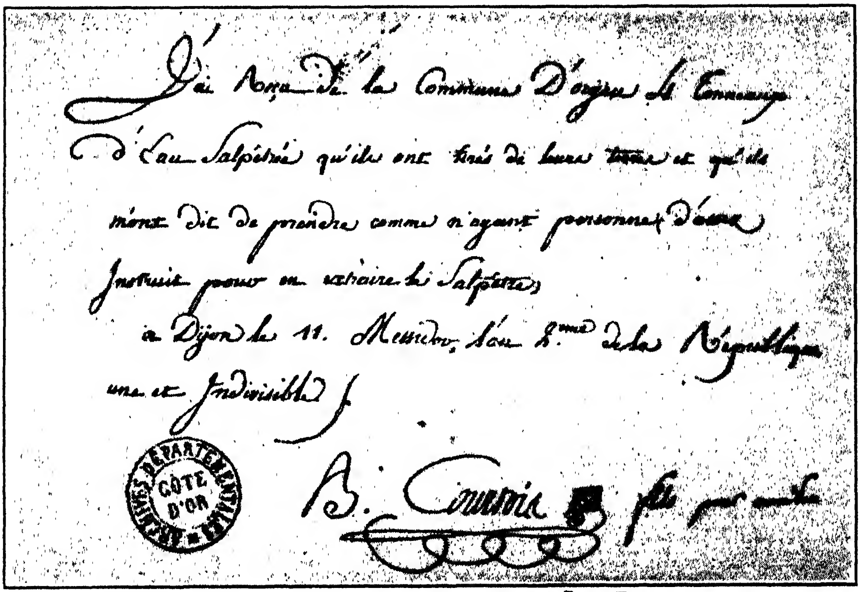
* The word *varech* is at present applied only to certain marine phanerogams used for packing and upholstering.

brown algae gathered at low tide, and by extracting the ash with water, Courtois obtained some mother liquors known as *salin de varech,* or *soude de varech.*

The algae that Courtois used yield an ash containing chlorides, bromides, iodides, carbonates, and sulfates of sodium, potassium, magnesium, and calcium. In his day, however, they were valued merely for their sodium and potassium compounds, which were recovered by burning the dried algae in longitudinal ditches along the seashore and leaching the ashes at the works.



J'ai Reçu de la Commune D'orgeu le Cinquante
C. d'eau Salpêtrée qu'ils ont tirés de leur terre et qu'ils
m'ont dit de prendre comme n'ayant personne d'assez
Instruit pour en extraire le Salpêtre
a Dijon le 11. Messidor, l'an 2me de la République
une et Indivisible
B. Courtois fils

From Toraude's
"Bernard Courtois et la Découverte de l'Iode"

AUTOGRAPH OF BERNARD COURTOIS (1794)

Translation: "I have received from D'orgeu township 50 casks of saltpeter solution which they have drawn from their property and which they have asked me to take because they have no one sufficiently trained to extract the saltpeter from it. Dijon the 11th of Messidor, the 2nd year of the Republic, one and indivisible. B. Courtois, son. . .". He was seventeen years old when he wrote this receipt.

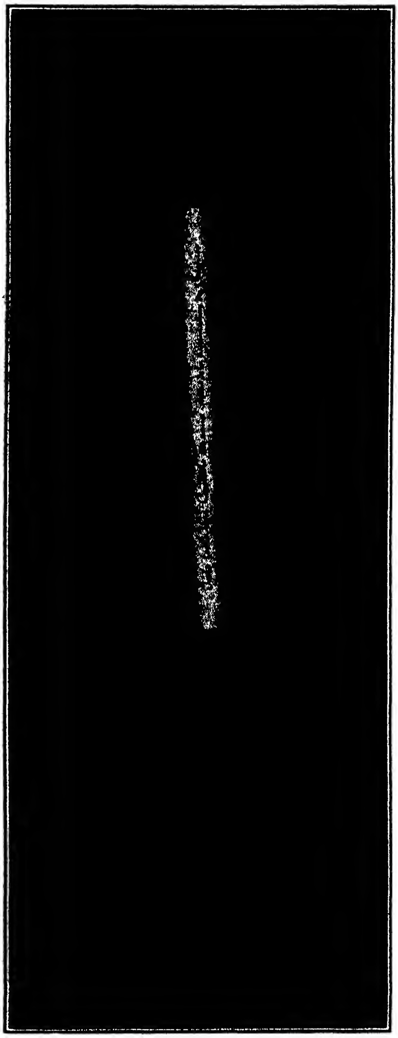
As evaporation proceeded, sodium chloride began to precipitate and later potassium chloride and potassium sulfate. The mother liquor then contained the iodides of sodium and potassium, part of the sodium chloride, sodium sulfate, sodium carbonate, cyanides, polysulfides, and some sulfites and hyposulfites resulting from the reduction of sulfates during calcination.

To destroy these sulfur compounds Courtois added sulfuric acid, and on one eventful day in 1811 he must have added it in excess (*54*). To his astonishment lovely clouds of violet vapor arose, and an irritating odor like that of chlorine permeated the room. When the vapors condensed on cold objects, no liquid was formed, but there appeared instead a quantity of dark crystals with a luster surprisingly like that of a metal (*45*).

Courtois noticed that the new substance did not readily form compounds with oxygen or with carbon, that it was not decomposed at red heat, and that it combined with hydrogen and with phosphorus. He observed that it combined directly with certain metals without effervescence and that it formed an explosive compound with ammonia. Although these striking properties made him suspect the presence of a new element, he was too lacking in self-confidence to attempt a thorough investigation in his poorly equipped laboratory and too poor to take the time from his business (*11*). He therefore asked two of his Dijon friends, Charles-Bernard Desormes and Nicolas Clément, Desormes' future son-in-law, to continue his researches in their laboratory at the *Conservatoire des arts et des métiers*, and allowed them to announce the discovery to the scientific world (*45*), (*55*).

In his famous research on the composition of sea water, J. G. Forchhammer stated that iodine was "the first element in sea water discovered not directly but by the analysis of the ashes of fucoidal plants, which by organic power had collected and concentrated it from sea water" (*98*).

Courtois was engaged for some years in the manufacture of iodine compounds and other chemical reagents, but in 1835 he was obliged to give up his business and go about the



From Toraude's "Bernard Courtois et la Découverte de l'Iode"

SEALED TUBE CONTAINING IODINE ISOLATED BY COURTOIS FROM THE MOTHER LIQUORS FROM THE PREPARATION OF SALTPETER

This tube, belonging to the Solvay Company of Belgium, was presented at the iodine centenary (Nov. 9, 1913) through the courtesy of M. C. Crinon.

city taking orders. According to Fremy, he prepared very pure iodine, gave specimens of it to his chemical friends, and noted its action on organic substances. Fremy also said:

> They have been unjust to Courtois in treating him as a simple saltpeter-maker; he was a very skilful chemist (un chimiste très habile); he ought to have been rewarded for his discovery of iodine, and not left to die in poverty (*12*), (*13*).

JEAN-ANTOINE-CLAUDE CHAPTAL, COMTE DE CHANTELOUP, 1756–1832

French physician, chemist, and manufacturer of saltpeter, soda, and beet sugar. Minister of the Interior under Napoleon. Author of books on chemical industry.

Courtois died in Paris on September 27, 1838. The Montyon prize of six thousand francs which the Royal Academy had awarded him in 1831 "for having improved the art of healing" had all been spent, and the widow, poor and uneducated, struggled against approaching deafness and blindness in a vain attempt to earn her living by lacemaking. It is indeed sad to know that her last months were spent in a charitable institution.

In the auditorium of the Dijon Academy, harmoniously decorated in the style of Louis XIV, there occurred on November 9, 1913,* a solemn civic ceremony in honor of the one hundredth anniversary of the discovery of iodine. At that time a commemorative plaque was placed on the birthplace of Courtois, and in the following year a street was named for him.

While Desormes devoted most of his time to applied chemistry, Clément (1779–1841) carried out a classical research in which he prepared the new substance and made a thorough study of its properties. In his report in 1813 he wrote:

> The mother liquor from seaweed ash contains quite a large quantity of a very peculiar and curious substance; it is easily extracted; one merely pours sulfuric acid on the mother liquor and heats the mixture in a retort the mouth of which is connected to a delivery-tube leading to a bulb. The substance which is precipitated in the form of a black, shining powder immediately after the addition of sulfuric

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* Although Courtois discovered iodine in 1811, the announcement by Clément and Desormes was not made until two years later. Therefore, the centenary was observed in 1913.

> acid, rises, when heated, in vapor of a superb violet color. This vapor condenses in the delivery-tube and receiver in the form of very brilliant crystalline plates having a luster equal to that of crystalline lead sulfide. Upon washing these plates with a little distilled water, one obtains the substance in the pure state (*45*), (*13*).

Clément believed iodine to be an element similar to chlorine (*12*), and showed it, first to Chaptal and Ampère, and later to Sir Humphry Davy. The proof of its elementary nature was given independently by Davy in England and by Gay-Lussac in France. Davy showed that iodine vapor is not decomposed by a carbon filament heated red-hot by a voltaic current (*12*), (*46*). In his classical research, the results of which were published in 1814, Gay-Lussac prepared hydrogen iodide and showed that it reacts with mercury, zinc, and potassium to give the corresponding metallic iodides, hydrogen, and no other product (*5*), (*39*).


Aesculape, 1913

JEAN-FRANÇOIS COINDET
1774–1834

Swiss physician who introduced the scientific use of iodine for treatment of goiter. Calcined sponge and other substances now known to contain iodine had long been used empirically for the same purpose. *See* ref. (*110*).

In 1820 Dr. Coindet of Geneva introduced the use of iodine in the treatment of goiter (*13*), (*56*). Long before this, however, it had been unknowingly used for this purpose in the form of ash from sponges. Jean-François Coindet was born at Geneva, Switzerland, in July, 1774. After completing his medical course at Edinburgh in 1797, he returned to Geneva, where he practiced for the rest of his life. In 1809 he became chief physician at the civil and military hospital. Although his large practice made heavy demands on his time and strength, Dr. Coindet never lost his active interest in scientific research.

One day in 1819*, when nineteen-year-old J.-B. Dumas had charge of the laboratory at the Le Royer pharmacy in Geneva, Dr. Coindet asked him to test some calcined sponge for iodine. When the boy obtained clear proof of its presence, Dr. Coindet asked him to suggest different forms in which iodine could be conveniently administered. Even before any iodide

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*** This is the date given by Van Tieghem, ref. (99); A. W. von Hofmann, ref. (103), gave the date as 1818 (when Dumas was only eighteen years old).**

was commercially available, Dumas proposed the tincture of iodine, potassium iodide, and a solution of iodine in potassium iodide. Two memoirs on this subject signed "A. Le Royer, pharmacist, and J.-B. Dumas, his pupil" were published in 1819 and 1820 in *Meisner's Journal* in Berne (*99*), (*100*).

In 1820 Dr. Coindet published in the *Annales de Chimie et de Physique* a paper entitled "Discovery of a new remedy for goiter" (*101*), (*102*). "A year ago," said he, "while looking for a formula in Cadet de Gassicourt's work, I found that Russel advised for goiter the use of kelp, *fucus vesiculosus*, under the name of *vegetable ethiops*. Not knowing then what relation might exist between this plant and the sponge, I suspected by analogy that iodine must be the active principle common to these two marine productions. . . . Up to the present, calcined sponge has formed the basis of all the remedies for goiter which have met with any success. It is Arnaud de Villeneuve who made it known" (*101*).

The earliest official recommendation of this remedy which the late Alexander Tschirch was able to find was in the eighth edition of the Augustana Pharmacopoeia of 1623 (*104*). The Chinese scholar Li Shi Chen, author of a famous pharmacopoeia (the Pen Ts'ao Kang Mu, sixteenth century A.D.), prescribed as a remedy for goiter a wine made from sea plants (*105*). In 1769 Dr. Russel recommended "vegetable ethiops" (charcoal made by burning fucoid seaweeds) for the same purpose (*13*).

As early as December, 1819, Dr. Johann Castor Straub, Professor of Chemistry at the Agricultural Institute at Hofwyl, Switzerland, noticed that calcined sponge (*spongia usta off.*) had an odor like that of iodine. He was soon able to demonstrate the presence in the sponge of this element, which had previously been detected only in marine plants. He therefore ascribed the medicinal value of the calcined sponge to its iodine content, and recommended the use of artificial substances containing iodine as specific for goiter (*104*), (*106*), (*107*).

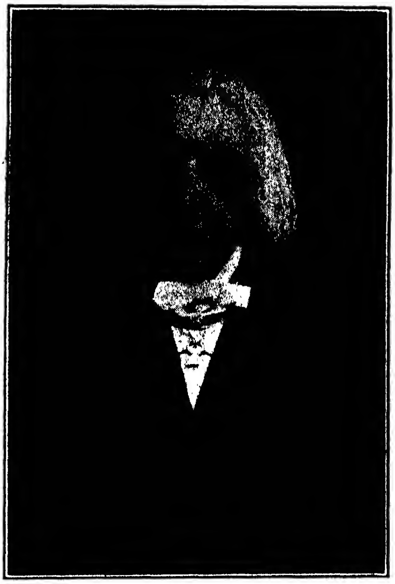
At about the same time, Dr. Andrew Fyfe (1792–1861) of Edinburgh detected iodine in several species of *Fucus*, in a species of conferva, and in "the common sponge of the shops," and published a paper on it in the *Edinburgh New Philosophical Journal* (*108*). After serving as assistant to Professor Hope, he gave private lectures on chemistry and pharmacy at Edinburgh. From 1844 until his death in 1861 he occupied the chair of chemistry at the University of Aberdeen (*109*).

Although calcined sponge often caused cramps of the stomach, Coindet found that sodium or potassium iodide made the goiters disappear much more quickly and without this deleterious effect. "What is the substance in the sponge which acts as a specific against goiter? It seemed probable to me," he continued, "that it was iodine; I was confirmed in that opinion when I learned that, near the end of 1819, M. Fife [Fyfe] of Edinburgh found iodine in the sponge; as early as six months ago I had confirmed its surprising effects in this malady" (*101*).

Dr. Coindet was one of the founders of the Medical Society of the Canton of Geneva, and was for many years its president. He was also elected and re-elected to the representative council of this canton. He died at Nice in 1834 (*102*), (*110*). His son, Dr. Charles W. Coindet, also published researches on the therapeutic uses of iodine (*105*), (*111*).

Bromine

Centuries before the element bromine was discovered, one of its organic compounds, Tyrian purple, was used as a rich costly dye prepared from a white juice secreted by the Mediterranean mollusk, the straight-spined Murex (*M. brandaris Linné*) (*91*). Strabo described the Tyrian dye-works in his *Geography*, and the product was mentioned frequently in the Bible (Ezek. 27, 7, 16) (*92*). In 1909 H. Friedländer of Vienna discovered that this royal dye from *Murex brandaris* is identical with the 6:6′ dibrom indigo which F. Sachs of Berlin and his collaborators had prepared only five years previously from *p*-bromo-*o*-nitrobenzaldehyde (*93*), (*94*), (*95*).



CARL LÖWIG*
1803–1890

Professor of chemistry at Heidelberg, Zurich, and Breslau. He prepared bromine in 1825, but before his investigation was completed Balard had announced the discovery. Löwig discovered bromine hydrate, bromal hydrate, and bromoform, and was the founder of the Silesian chemical industry and of the Goldschmieden alumina works at Deutsch-Lissa.

In 1825 Carl Löwig, a new student who had just entered the chemical laboratory at Heidelberg, won the immediate interest of Leopold Gmelin, his professor. Löwig had brought with him from his home at Kreuznach a red liquid which he had prepared by passing chlorine into the mother liquor from a salt spring and shaking it out with ether. The red liquid had remained after he had distilled off the ether. Professor Gmelin asked him to prepare more of it in order to study its properties, but in the meantime there appeared in 1826 in the

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* The author is indebted to the late Dr. Max Speter of Berlin and Dr. Julius Meyer of Breslau for their assistance in obtaining this portrait, the original of which hangs in the Chemical Institute at Breslau. Some valuable information about Löwig's scientific activities was also graciously contributed by Professor Meyer.

Annales de chimie et de physique a paper by Balard announcing the discovery of bromine (*28*), (*36*), (*57*). The properties which Balard ascribed to bromine were identical with those Löwig had observed for the substance from Kreuznach. This explains why Balard, instead of Löwig, is regarded as the discoverer of bromine.

Carl Löwig was born at Kreuznach on March 17, 1803. In his youth he studied pharmacy, but his later study was confined entirely to chemistry. He continued his investigation of the compounds of bromine for several years, and in 1829 published a monograph on "Bromine and Its Chemical Relations."

In 1833 he was called to the newly founded University of Zurich, where, in spite of the very meager equipment, he analyzed many Swiss mineral waters and published monographs on them. His "*Chemie der organischen Verbindungen*," based on the radical theory, "was the Beilstein of that time, and was to be found in the hands of every chemist" (*57*), (*66*).

In 1853 Löwig became Bunsen's successor at Breslau. He was given offices of great responsibility, and served as Rector both at Zurich and at Breslau. He taught six semesters at Heidelberg, forty at Zurich, and seventy-two at Breslau, and hoped to teach two more in order to make the total one hundred and twenty. This hope was not to be realized, however, for, while walking in the zoölogical garden, he failed to notice some steps, fell, and received a fracture of the hip from which he never recovered. He died on March 27, 1890, ten days after his eighty-seventh birthday (*57*).

Antoine-Jérôme Balard (*14*), was born at Montpellier on September 30, 1802. Since his parents were poor, he was adopted and educated by his godmother. He studied at the College of Montpellier for a time, and at the age of seventeen years he became a *préparateur* at the *École de Pharmacie*, where he graduated in 1826 (*47*), (*66*), (*68*).

In 1824, while studying the flora of a salt marsh, he noticed a deposit of sodium sulfate which had crystallized out in a pan containing mother liquor from common salt. In an attempt to find a use for these waste liquors he performed a number of experiments, and noticed that when certain reagents were added, the mother liquor became brown. His investigation of this phenomenon, made when he was only twenty-three years old, led to the remarkable discovery which Dulong described in the following letter to Berzelius written on July 1, 1826:

> .... But here is another piece of recent news... It is a new simple body which will find its place between chlorine and iodine. The author of this discovery is M. Ballard of Montpellier. This new body, which he calls *muride*, is found in sea water. He has extracted it from the mother liquor of Montpellier brines by saturating them with chlorine and distilling. He obtains a dark red liquid substance boiling at 47°. The vapor resembles that of nitrous acid. Its specific gravity is 3. One preserves it under concentrated sulfuric

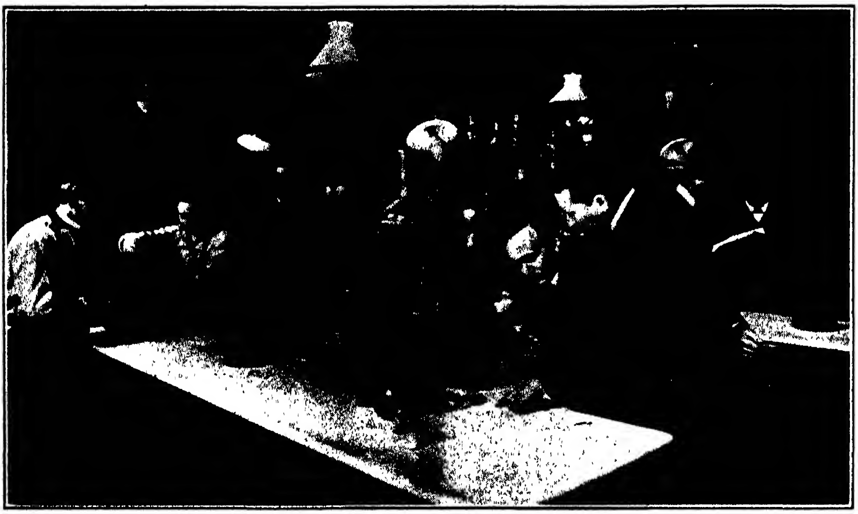
Antoine-Jérôme Balard, 1802–1876

French chemist and pharmacist who discovered bromine. Professor of chemistry at the Sorbonne and at the Collège de France. He discovered hypochlorous acid, worked out the constitution of Javelle water, and perfected industrial methods for extracting various salts from sea water.

> acid. It combines with metals and gives compounds sensibly neutral, of which several are volatile, notably the muride of potassium. . . (*15*).

Since the name *muride* did not find favor with the French Academy's committee, consisting of Vauquelin, Thenard, and Gay-Lussac, the element is now known as *bromine*, meaning *bad odor* (*12*), (*26*).

When Balard made this eventful discovery, he was merely an obscure young assistant in the chemistry department of his college. He had noticed that when the lye from the ash of *Fucus* was treated with chlorine water and starch, two layers appeared in the solution. The lower layer was blue because of the action of the starch on the iodine, and the upper one was intensely yellow.



ONE OF THE LABORATORIES OF MINERALOGICAL CHEMISTRY AT THE SORBONNE

Balard, the discoverer of bromine, Moissan, the discoverer of fluorine, Lamy who isolated thallium, and M. and Mme. Curie, the discoverers of radium all taught at the Sorbonne.

The young assistant concluded that there were only two possible explanations: The yellow substance must either be a compound of chlorine with some constituent of the lye, or it must be a new element just liberated from one of its compounds by the chlorine, which had replaced it. Balard at first favored the first hypothesis and thought that he had an iodide of chlorine, but, when all attempts to decompose the new substance failed, he concluded that his second explanation must be the correct one and that the new element must be similar to iodine and chlorine (*28*).

He afterward found that bromine can be shaken out of solution, first with ether and then with caustic potash. Upon heating the resulting potassium bromide with sulfuric acid and manganese dioxide, the bromine can be distilled off and condensed as a red liquid or collected in water (*12*). Just as mercury is the only common metal whose liquid phase is stable at room temperature, bromine is the only liquid non-metal.

The French Academy's report of the Procès-verbal of Monday, August 14, 1826, signed by Vauquelin, Thenard, and Gay-Lussac, reads as follows:

> If the few experiments which we have been able to perform have not afforded us that certainty of the existence of bromine as a very simple body which in the present day is properly required, we consider it at least very probable that it is so. The memoir of M. Balard is extremely well drawn up, and the numerous results which he relates would not fail to excite great interest, even if it should be proved that bromine is not a simple body. The discovery of bromine is a very important acquisition to chemistry, and gives M. Balard honorable rank in the career of the sciences. We are of the opinion that this young chemist is every way worthy of the encouragement of the Academy, and we have the honor to propose that his memoir shall be printed in the *Recueil des Savants Étrangers* (*16*), (*29*).

In 1842 Balard succeeded Thenard at the Sorbonne, and in 1851 he accepted a professorship at the Collège de France (*36*). He discovered hypochlorous acid, worked out the constitution of Javelle water (*44*), and perfected industrial methods for the extraction of various salts from sea water. He worked for twenty years at these technical researches, and extracted sodium sulfate, the basis of the soda industry, directly from sea water. He also extracted potassium salts from the sea water, and his artificial potash, entering into competition with that from the ashes of plants, soon lowered the price. Before the discovery of the Stassfurt deposits in 1858, all the bromine used by photographers was prepared by Balard's method.

The memory of his early poverty made Balard economical in his researches and ascetic in his manner of living. Although he survived his three children and his wife, his stepchildren were a great consolation to him in his old age. He died in 1876, honored because of his achievements and loved because of his generosity, modesty, and warmth of heart (*47*). In his eulogy, J.-B. Dumas mentioned Balard's love for the sea: "His thinking always drew him to the sea; he would have liked to live near it, he said, in order to fathom its chemical history; and, as soon as a free moment permitted, he took the train to become elated by the effluvia of the Mediterranean" (*96*).

The glory due to Balard for his discovery of bromine is enhanced when one knows that the great Liebig just missed it. Several years before, a German firm had asked Liebig to examine the contents of a certain bottle, and he had concluded, without thorough study, that the substance was iodine chloride. When he heard of the discovery of bromine, he immediately recognized his error and placed the bottle in a special case which he called his "cupboard of mistakes" (*11*). Hence, when his dear friend Wöhler a few years later just missed discovering vanadium,* Liebig knew how to sympathize with him.

As soon as he had read Balard's paper on bromine, Liebig examined the brine from Theodorshalle near Kreuznach and prepared nearly twenty grams of bromine. His experiments led him to conclude, as Balard had done, that it must be a simple substance (*27*). "I know a chemist," said he, years later (referring to himself), "who during a visit to Kreuznach occupied himself with the investigation of the saline mother liquors there; he found iodine in them and observed that the iodine-starch, when left over night, acquired a fire-yellow color. . . . A few months later, he received Herr Balard's beautiful research and was in a position that very day to make known a series of experiments on the relation of bromine to iron, platinum, and carbon; for Balard's bromine stood in his laboratory labeled *liquid iodine chloride.* Since then he makes no more theories unless they can be directed and supported by unambiguous experiments" (*97*). Liebig's first paper on bromine was published in the *Annales de chimie et de physique* in 1826 (*27*).

Fluorine

In his *Bermannus*, Georgius Agricola in 1529 described the use of fluorspar as a flux: "*Bermannus.*—These stones are similar to gems, but less hard. . . . Our miners call them *fluores*, not inappropriately to my mind, for by the heat of fire, like ice in the sun, they liquefy and flow away. They are of varied and bright colors. . . . *Anton.*—What is the use of *fluores? Bermannus.*—They are wont to be made use of when metals are smelted, as they cause the material in the fire to be much more fluid. . ." (*70*).

In 1676 Johann Sigismund Elsholtz (or Elsholz) informed the members of the Imperial Society for Investigating Nature (Societati Imperiali Naturae Curiosorum) "that he was acquainted with a phosphorus which had its light neither from the sun nor from fire, but which, when heated on a metal plate over glowing coals, shone with a bluish-white lustre; so that by strewing the powder of it over paper, one might form luminous writing" (*71*), (*72*).

In his history of the discovery of phosphorus, G. W. Leibniz stated in 1710: "I also showed this inquisitive prince [Duke Johann Friedrich] another kind [of phosphorus] which one might call *thermophosphorus.* One draws letters and figures, for example, on an iron plate with a certain flux in the mines; lays the plate on glowing coals; whereupon they shine, even though the plate is not heated to redness" (*73*). An editorial footnote to this article in *Crell's Neues chemisches Archiv* in 1784 stated that this flux was undoubtedly fluorspar.

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* See Chapter XI, pp. 194–6.

As early as 1670 Heinrich Schwanhard of Nuremberg, a member of a famous family of glass cutters, found that when he treated this mineral with strong acids, the lenses of his spectacles became etched (*71*), (*74*). This led him to discover and perfect a new means of etching glass without a diamond or any abrasive. In his "History of Inventions," Johann Beckmann described the process as follows: "At present," said he, "the glass is covered with a varnish, and those figures which one intends to etch are traced out through it; but Schwanhard, when the figures were formed, covered them with varnish, and then by his liquid corroded the glass around them; so that the figures, which remained smooth and clear, appeared when the varnish was removed, raised from a dim or dark ground" (*71*). Schwanhard raised this art to a high degree of perfection, and depicted people, animals, flowers, and herbs in relief on the glass (*75*). He did this work only for Emperor Charles II.

The formula for Matthäus Pauli's glass-etching fluid was made public in 1725 (*76*). Beckmann then quoted the following recipe from page 107 of the *Breslauer Sammlung zur Natur- und Medicin-Geschichte* for January, 1725: "When *spiritus nitri per distillationem* has passed into the recipient, ply it with a strong fire, and when well dephlegmated, pour it, as it corrodes ordinary glass, into a Waldenburg flask; then throw into it a pulverized green Bohemian emerald, otherwise called ***hesphorus*** (which, when reduced to powder and heated, emits in the dark a green light, and place it in warm sand for twenty-four hours. . ." (*71*), (*74*). The "Bohemian emerald" was undoubtedly green fluorspar. Fredrick·Accum published an article in *Nicholson's Journal* for 1800 on the antiquity of the art of etching by means of hydrofluoric acid (*74*).

In 1768 A. S. Marggraf made the first chemical investigation of fluorite, distinguished it from heavy spar and selenitic spar (sulfates of barium and calcium), and showed that it is not a sulfate (*77*), (*78*). When he distilled pulverized fluorspar with sulfuric acid from a glass retort, the glass was badly attacked and even perforated. He noticed that an "earth" [silica] appeared in the receiver, and therefore concluded that the sulfuric acid had liberated a volatile earth from the fluorspar (*77*).

In 1771 Scheele investigated a green variety of fluorspar from Garpenberg and a white one from Gislöf in Scania. He found that the green specimen contained a trace of iron but that the white one did not. When he heated the pulverized mineral with oil of vitriol [sulfuric acid], he noticed that the inner surface of the glass retort became corroded, that the white solid mass left at the bottom consisted mainly of selenite [calcium sulfate], and that an acid passed over into the receiver. He concluded that fluorspar "consists principally of calcareous earth saturated with a specific acid" (*79*). By adding lime water to a dilute solution of this acid, he synthesized an artificial fluorspar which, like the natural mineral, phosphoresced when warmed in the dark.

Scheele stated that the acid of fluorspar [hydrofluoric acid] can dissolve siliceous earth and that therefore it is almost impossible to prepare the pure acid. He believed that the earthy deposit in the receiver (Marggraf's "volatile earth") was siliceous earth produced by a reaction between the "acid of fluorspar" and water. In 1778 his friend Friedrich Ehrhart, a botanist at Hanover who had studied under Carl von Linné and T. Bergman, wrote Scheele that this deposit had merely been dissolved from the glass retort. When J. K. F. Meyer of Stettin repeated the experiment using a lead retort instead of a glass one, he found no such deposit in the receiver (*80*). Carl Friedrich Wenzel with a lead retort and Giovanni Antonio Scopoli with a gold-plated silver one obtained similar results (*76*). In 1781 Johann Christian Wiegleb proved quantitatively that the silica came from the glass retort, and in the same year Scheele became convinced of his error (*77*), (*81*), (*82*). These results were also confirmed by Wilhelm Heinrich Sebastian Bucholtz (*83*). In 1780 and again in 1786 (the last year of his life), Scheele published papers defending his claim that fluorspar contains a peculiar acid (*79*).

ANDRÉ-MARIE AMPÈRE
1775–1836

French physicist, mathematician, and chemist. Professor at the École Polytechnique, Paris One of the founders of electrodynamics. Inventor of the astatic needle. The practical unit of current strength was named for him.

The new acid immediately aroused widespread interest. John Hill, in the notes to his translation of Theophrastus's "History of Stones," stated in 1774: "There exists in the Mineral World a native acid; and probably only one; tho' it exhibits itself under different Forms. Of the existence of this we are certain; altho' we never have seen it pure; nor can. It never becoming an Object of our Senses, but in Mixture with other Bodies. It has been called the Vague Acid and the Universal Acid. We have been accustomed to meet with it under two distinct Forms; and to know it under the Names of two Species: These are the Vitriolic and the Muriatic Acid: and to these we are lately taught to add a third, which, from the Place where it has been discovered, Authors have called the Swedish Acid; and to which some, tho' very improperly, have given the Name of the Sparry

Acid. Perhaps, in distinction from the other two, it may be better named the Stony Acid" (*84*), (*85*).

In 1786 M. H. Klaproth published in *Crell's Annalen* a method devised by Count von Gesler for etching letters and drawings on glass with hydrofluoric acid (*76*), (*86*), and in 1788 Jean-Pierre-Casimir de Marcassus, Baron de Puymaurin (1757–1841) published a similar process in the *Mémoires de Toulouse* (*87*), (*88*), (*89*). The German translation of Macquer's chemical dictionary, published in 1790, contains a detailed account of it (*88*). Stephen Weston mentioned the hydrofluoric acid etchings of Puymann [Puymaurin?] and stated in 1805 that "the best work of this kind is that which represents Chemistry weeping over the tomb of Scheele, the discoverer of the fluoric [hydrofluoric] acid" (*90*)

The history of fluorine gas is a tragic record. Lavoisier, it will be recalled, thought that all acids contain oxygen, but Davy showed that "fluoric" hydrofluoric acid does not. Ampère suggested to Davy that it must be a compound of hydrogen and an unknown element (*31*), (*32*). Paul Schützenberger expressed the belief that this unknown substance, fluorine, would be found to be the most active of all the elements, and correctly predicted some of its properties (*18*), (*19*). It is this extreme activity of the element that made its liberation such a difficult and dangerous task and brought agony and death to some of the pioneer investigators.

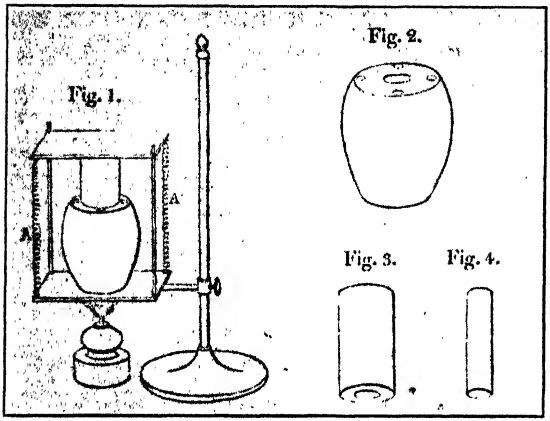
Davy, Gay-Lussac, and Thenard all suffered intensely from the effects of inhaling small quantities of hydrogen fluoride. Davy found that his silver and platinum containers were attacked, but believed that fluorine could be liberated if a fluorspar vessel were used (*23*), (*30*), (*62*). Two members of the Royal Irish Academy, George Knox and his brother, the Reverend Thomas Knox, of Toomavara, Tipperary, made an ingenious apparatus of fluorspar. They were unable, however, to collect and study the gas. Both suffered the frightful torture of hydrofluoric acid poisoning (*20*). The Reverend Thomas Knox nearly lost his life, and George Knox had to rest

PAULIN LOUYET
1818–1850

Belgian chemist who investigated the compounds of fluorine. For his attempts to liberate fluorine, the Knox brothers placed at his disposal their costly fluorspar and platinum equipment. His premature death was caused by continued exposure for about a decade to the toxic compounds of this element (*69*). Engraving by Danse, Brussels, 1851.

in Naples for three years in order to regain his health (*40*). P. Louyet of Brussels, although fully aware of the Knox brothers' misfortune, continued his dangerous researches too long, and died a martyr to science (*17*), (*18*), (*40*), (*42*). Professor Jérôme Nicklès of Nancy met a similar fate (*35*), (*43*), (*60*), (*67*).

Edmond Fremy, who had watched Louyet perform some of his experiments (*33*), tried to decompose anhydrous calcium fluoride electrolytically, and did obtain calcium at the cathode, while a gas, which must have been fluorine, escaped at the anode (*34*). However, because of its tendency to add on to other substances and form ternary and quaternary compounds, Fremy failed in all his attempts to collect and identify the gas. When he allowed chlorine to act on a fluoride, he obtained no fluorine, but only a fluochloride; when he used oxygen in place of chlorine, he obtained an oxyfluoride.



Philosophical Magazine, 1836

APPARATUS USED BY THE KNOX BROTHERS IN THEIR ATTEMPTS TO LIBERATE FLUORINE

Upon treating dry "fluoride of mercury" with dry chlorine they obtained crystals of mercuric chloride. A piece of gold foil which had been acted on by the gas in the receiver was placed on glass and treated with sulfuric acid. Since the glass was attacked, they concluded that fluorine had been liberated and had formed gold fluoride. No hydrogen was detected.

Fig. 1. Fluorspar vessel in the stand which holds down the receiver by means of spiral springs.

Fig. 2. Vessel with cover off, showing the orifice and the small depressions containing gold leaf.

Fig. 3. Receiver. Fig. 4. Stopper.

This seemingly hopeless field of experimentation was soon abandoned, but in 1869 the English chemist, George Gore, liberated a little fluorine, which immediately combined explosively with hydrogen (*18*), (*35*). When he tried to electrolyze anhydrous hydrofluoric acid "with anodes of gas-carbon, carbon of lignum-vitae, and of many other kinds of wood, of palladium, platinum, and gold, . . . the gas-carbon disintegrated rapidly, all the kinds of charcoal flew to pieces quickly, and the anodes of palladium, platinum, and gold were corroded without evolution of gas" (*35*). Moissan mentioned the "remarkable exactitude" of Gore's memoir (*23*).

The apparently impossible task was finally accomplished by Moissan in 1886. Ferdinand-Frédéric-Henri Moissan was born at 5, Rue Montholon in Paris on September 28, 1852. When he was twelve years old, the family

EDMOND FREMY
1814–1894
Professor of chemistry at the École Polytechnique and director of the Muséum d'Histoire Naturelle. He electrolyzed anhydrous calcium fluoride but could not collect the fluorine. He was present, however, when his former pupil, Henri Moissan, exhibited the new gas before a committee from the Academy of Sciences. Fremy wrote a monograph on the synthesis of rubies. See J. CHEM. EDUC., **8**, 1017–9 (June, 1931) for illustrations of his artificial rubies.

DR. GEORGE GORE,† 1826–1908
English electrochemist. Head of the Institute of Scientific Research, Easy Row, Birmingham. He improved the art of electroplating and wrote treatises on "The Art of Electrometallurgy" and "The Electrolytic Separation and Refining of Metals." His estate was bequeathed to the Royal Society of London and the Royal Institution of Great Britain.

moved to the little town of Meau in the department of Seine-et-Marne, where he attended the municipal college. His first lessons in chemistry were received from his father, a railroad official (*22*), (*58*).

Obliged to leave school at the age of eighteen years, he became an apprentice in the Bandry apothecary shop located at the intersection of Rue Pernelle and Rue Saint Denis in Paris. Here his ready knowledge of chemistry enabled him to save the life of a man who had swallowed arsenic in an attempt at suicide (*21*), (*22*). In 1872 Moissan decided to give up his position at the pharmacy in order to study under Edmond Fremy at the Musée d'Histoire Naturelle. Here he not only made rapid progress in chemistry and pharmacy, but also became a connoisseur of art and literature, and even wrote a rhymed play which was almost accepted for the audiences at the Odéon. He was afterward able to laugh at this early disappointment and to say, "I believe I did better to study chemistry"*(*22*).

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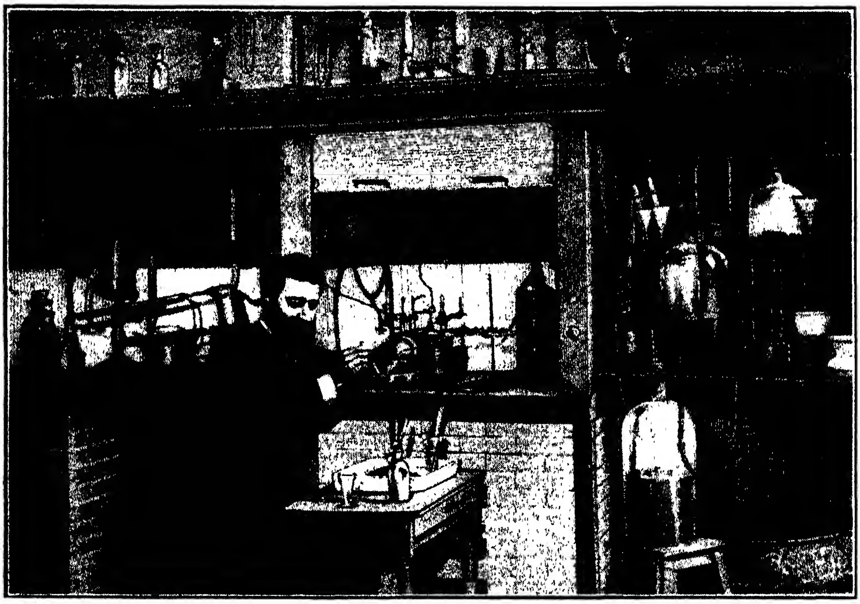
* "Je crois que j'ai mieux fait de faire de la chimie."

† This portrait was obtained through the courtesy of Mr. R. B. Pilcher, Registrar and Secretary of the Institute of Chemistry of Great Britain and Ireland.

In 1879 he passed his examination for first-class pharmacist and accepted a position at the École Supérieure de Pharmacie (*21*), (*58*).

Three years later there occurred in Moissan's life a most fortunate event—his marriage to Léonie Lugan. She proved to be a devoted wife and comrade, a hospitable, charming hostess, and a great help to him in his scientific work. M. Lugan was also an ideal father-in-law, in full sympathy with Moissan's scientific researches. He gladly provided material support for his daughter's family, and urged Moissan to devote all his time to science, unhampered by financial worries. Since the latter had no laboratory at the School of Pharmacy, he did his first experimental work in a building situated on the Rue Lancry, but Debray afterward allowed him to use the more powerful battery in a temporary barracks on the Rue Michelet (*22*).



PROFESSOR MOISSAN PREPARING FLUORINE IN HIS LABORATORY AT THE ÉCOLE DE PHARMACIE IN PARIS*

Fremy had concluded from his experiments that fluorine had probably been liberated in the electrolysis of the fluorides of calcium, potassium, and silver, but that, because the temperature had been too high, it had immediately attacked the container. He prepared anhydrous hydrogen fluoride,

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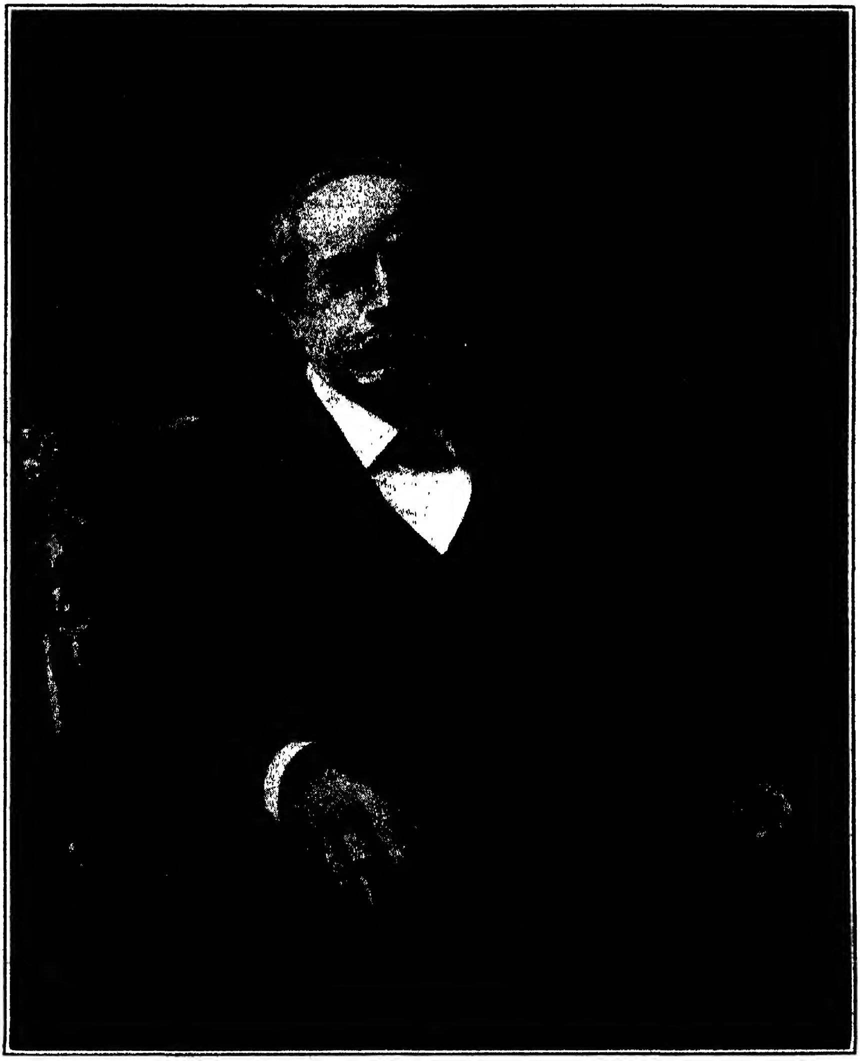
* The picture of Moissan preparing fluorine has been reproduced from an article by GASTON TISSANDIER, *La Nature*, 18, [1], 177 (Feb. 22, 1890), by permission of Masson et Cie., Éditeurs, Paris.



PIERRE-EUGÈNE-MARCELIN BERTHELOT, 1827–1907

French chemist and historian of chemistry. His researches were in the diverse fields of organic synthesis, chemical statics and dynamics, thermochemistry, explosives, nitrifying bacteria in the soil, and the oriental sources of alchemy. In his early days he assisted Balard at the Collège de France and many years later he served on a committee with Debray and Fremy to investigate Moissan's discovery of fluorine.

but found himself caught in the horns of the following dilemma: when *moist* hydrogen fluoride was electrolyzed, he obtained only hydrogen, oxygen, and ozone; and dry hydrogen fluoride would not conduct the current (*22*).

Moissan reasoned that if he were trying to liberate chlorine he would not choose a stable solid like sodium chloride, but a volatile compound like hydrochloric acid or phosphorus pentachloride. His preliminary experiments with silicon fluoride convinced him that this was a very stable compound, and that, if he should ever succeed in isolating fluorine, it would unite with silicon with incandescence, and that therefore he might use silicon in testing for the new halogen. After many unsuccessful attempts to electrolyze phosphorus trifluoride and arsenic trifluoride, and after four interruptions caused by serious poisoning, he finally obtained powdered arsenic at the cathode and some gas bubbles at the anode. However, before these fluorine bubbles could reach the surface, they were absorbed by the arsenic trifluoride to form the pentafluoride (*18*), (*23*).

Moissan finally used as electrolyte a solution of dry potassium acid fluoride in anhydrous hydrofluoric acid. His apparatus consisted of two platinum-iridium electrodes sealed into a platinum U-tube closed with fluorspar screw caps covered with a layer of gum lac (*42*), (*49*), (*59*). The U-tube was chilled with methyl chloride, the gas now used in many modern refrigerators, to a temperature of −23°.

Success finally came. On June 26, 1886, a gas appeared at the anode, and when he tested it with silicon, it immediately burst into flame. Two days later he made the following conservative announcement to the Academy:

> One can indeed make various hypotheses on the nature of the liberated gas; the simplest would be that we are in the presence of fluorine, but it would be possible, of course, that it might be a perfluoride of hydrogen or even a mixture of hydrofluoric acid and ozone sufficiently active to explain such vigorous action as this gas exerts on crystalline silicon (*42*).

This announcement was read to the Academy by Debray, for Moissan was not then a member, and the president appointed a committee consisting of MM. Debray, Berthelot, and Fremy to investigate the discovery. In the presence of these distinguished guests, the apparatus acted like a spoiled child. Moissan could not obtain as much as a bubble of fluorine. However, on the following day he used fresh materials and demonstrated his discovery to the entire satisfaction of the committee (*22*). Thus Fremy, who had come so near to making this discovery himself, was able to say with all sincerity, "A professor is always happy when he sees one of his students proceed farther and higher than himself" (*60*).

ALFRED E. STOCK

Former director of the Chemical Institute of the Technische Hochschule of Karlsruhe. Former student of Henri Moissan and author of an excellent biographical sketch of him. Visiting lecturer at Cornell University in 1932. He is an authority on the high-vacuum method for studying volatile substances, the chemistry of boron, the preparation and properties of beryllium, and chronic mercurial poisoning.

The successful isolation of fluorine made Moissan's name known throughout the scientific world, and in 1893 another achievement won for him more popular publicity than he desired. On February sixth of that year he succeeded in preparing small artificial diamonds by subjecting sugar charcoal to enormous pressure (*52*), (*53*), (*63*). Most of his diamonds were black like carbonado, but the largest one, 0.7 of a millimeter long, was colorless. His colleagues affectionately named this little diamond "The Regent," for to them it was as precious as the 137-carat specimen in the Louvre (*22*).

Moissan's electric furnace was a valuable incentive to research. With its aid he prepared many uncommon metals such as uranium, tungsten, vanadium, chromium, manganese, titanium, molybdenum, columbium, tantalum, and thorium, much of this work being done at the Edison Works on Avenue Trudaine (*24*), (*61*). As a practical result of her husband's researches, Mme. Moissan was one of the first women in the world to use aluminum cooking utensils (*22*).

Moissan always insisted on extreme neatness in his laboratory, and the wooden floors were waxed every Saturday. Alfred Stock (*64*) relates that one day Professor Moissan looked critically at the floor and said reproachfully, "Who did that?" Upon careful examination, Dr. Stock noticed that a few drops of water from the tip of his wash-bottle had fallen to the waxed floor (*22*).

Moissan was one of the most polished scientific lecturers in Paris. His ease of delivery, his well-modulated voice, his carefully chosen experiments, and his gentle humor attracted great crowds to his lectures at the Sorbonne. At exactly five o'clock the two large doors of the lecture room used to be opened simultaneously by two servants, and at a quarter past five the lecture began. Then for an hour and a quarter Moissan held the eager attention of his audience. Sir William Ramsay said of him, His command of language was admirable; it was French at its best. The charm of his personality and his evident joy in exposition gave keen pleasure to his auditors. He will live long in the memories of all who were privileged to know him, as a man full of human kindness, of tact, and of true love for the subject which he adorned by his life and work (*22*), (*48*).

HENRI MOISSAN
1852–1907

Professor of chemistry at the École Supérieure de Pharmacie. The discoverer of the element fluorine. With his electric furnace he prepared many uncommon metals such as uranium, tungsten, and vanadium.

Moissan had an artistic, hospitable home in the quiet Rue Vauquelin, and was proud of his Corot landscape and his fine collection of autographs. M. and Mme. Moissan and their son Louis usually spent their vacations traveling in Italy, Spain, Greece, the Alps, or the Pyrenees, and in 1904 Moissan came to America to visit the St. Louis World's Fair (*22*).

His life was undoubtedly shortened by his continued work with the toxic gases, fluorine and carbon monoxide. He died on February 20, 1907. His only child, Louis, an assistant at the École de Pharmacie, who was killed on a battlefield of World War I, left 200,000 francs to the school for the establishment of two prizes: the Moissan chemistry prize in memory of his father and the Lugan pharmacy prize in honor of his mother (*25*), (*65*).

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XXV. THE INERT GASES

In 1894 Lord Rayleigh and Sir William Ramsay startled the scientific world by announcing the discovery of a new elementary, gaseous constituent of the atmosphere. Thorough investigation of the properties of the new element, which they called argon, has shown that it has scarcely any tendency whatsoever to form chemical compounds. Another closely related gas was revealed in a manner no less dramatic. In 1868 the astronomers, Jules Janssen and Sir Norman Lockyer, had independently observed in the sun's spectrum a yellow line, D_3, *which did not belong to any element then known to exist on the earth, and Lockyer had therefore postulated the existence of a solar element, helium. In 1895 Ramsay in England and Cleve and Langlet in Sweden independently discovered helium in a radioactive mineral. The researches of Ramsay and Travers soon revealed three other gases, neon, krypton, and xenon, which, since they show almost no tendency to unite with other elements, are classified with argon and helium in the aristocratic family of the noble gases.* Radon, the heaviest member of the group, will be discussed in Part XXVI with the radioactive elements.*

. . . . . .

> *Accurate and minute measurement seems to the non-scientific imagination a less lofty and dignified work than looking for something new. But nearly all the grandest discoveries of science have been but the rewards of accurate measurement and patient long-continued labor in the minute sifting of numerical results* (*1*).

Until the closing years of the nineteenth century chemists believed that the atmosphere had been thoroughly investigated, and no one thought for a moment of searching there for new elements. It is true, however, that Mr. Henry Cavendish had long before predicted the discovery of an unknown gas in the atmosphere, for in 1785 he had passed electric sparks through a mixture of oxygen and common air in the presence of alkali ("soap-lees"), and had found that part of the "phlogisticated air" (nitrogen) had failed to be oxidized and absorbed. He had said that this residue was "certainly not more than $^1/_{120}$ of the bulk of the phlogisticated air let up into the tube; so that if there is any part of the phlogisticated air of our atmosphere which differs from the rest and cannot be reduced to nitrous acid, we maysafely conclude that it is not more than $^1/_{120}$ part of the whole" (*2*). This important experiment had long been forgotten by chemists, but in 1882 Lord Rayleigh began a research on the densities of the gases in the atmosphere.

Robert John Strutt, the third Lord Rayleigh, was born at Terling on November 12, 1842. His ability for clear thinking and self-expression was evident in his student days, and when he was Senior Wrangler in the

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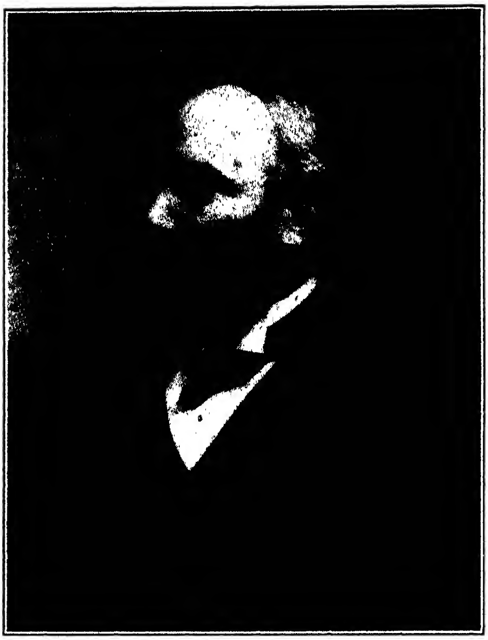
* A few compounds of the elements of this group have been reported in chemical literature.



Courtesy of the late L. C. Newell

ROBERT JOHN STRUTT, THE THIRD LORD RAYLEIGH, 1842–1919

Professor of physics at Cavendish Laboratory, Cambridge. He made elaborate investigations of the electrochemical equivalent of silver and of the combining volumes and compressibilities of gases. His observation that nitrogen prepared from the atmosphere is heavier than nitrogen prepared from ammonia led to the discovery of argon, the first noble gas. He also contributed to optics and acoustics.

Tripos in 1865, one of his examiners remarked, "Strutt's papers were so good that they could have been sent straight to press without revision" (*41*).

After the great physicist Clerk Maxwell died in 1879, Lord Rayleigh became his successor at the Cavendish Laboratory, Cambridge. During his professorship the classes increased in size, and women from Girton and Newnham colleges were for the first time admitted on the same terms as the men. Since he was allowed insufficient funds for the purchase of new apparatus, he contributed £500 of his own money and solicited his friends for similar contributions until he had collected £1500 (*3*).

In 1882 Lord Rayleigh told the British Association that he had begun an investigation of the densities of hydrogen and oxygen to find out whether or not the ratio is exactly 1 to 16; and ten years later he announced that the correct ratio is 1 to 15.882 (*38*). In the course of this elaborate research on the combining volumes and compressibilities of gases, made with a view to calculating their molar volumes under limiting conditions, Lord Rayleigh also measured the density of nitrogen (*40*).

Although the oxygen which he prepared by three different methods all had the same density, his results with nitrogen were puzzling. The nitrogen he prepared from ammonia was always lighter by about five parts in one thousand than that which he prepared by absorbing the oxygen, carbon dioxide, and moisture from atmospheric air. He then wrote to the English magazine, *Nature*, asking the readers to submit explanations, but none were received (*39*).

Lord Rayleigh himself thought of four possible explanations: (1) the nitrogen he had prepared from the atmosphere might still contain some oxygen; (2) the nitrogen prepared from ammonia might be slightly contaminated with hydrogen; (3) the nitrogen from the atmosphere might contain some N_3 molecules analogous to ozone; or (4) some of the molecules in the nitrogen from ammonia might have decomposed and thus decreased the density of the gas (*40*), (*45*).

Courtesy Lady Ramsay

SIR WILLIAM RAMSAY, 1852–1916

Scottish chemist and physicist. Discoverer of the inert gases. Lord Rayleigh was a co-discoverer of argon, and M. W. Travers collaborated in the discovery of krypton, neon, and xenon. After F. E. Dorn had discovered radon, or radium emanation, Ramsay and Whitlaw Gray determined its density and proved it to be the heaviest member of the argon family.

The first hypothesis was most improbable, for, because of the very slight difference in the densities of oxygen and nitrogen, the contamination would have had to be very great in order to account for the discrepancy of five parts in one thousand. Lord Rayleigh showed experimentally that the nitrogen prepared from ammonia was entirely free from hydrogen. The third hypothesis was not encouraging, for he was unable to increase the density of his nitrogen by passing a silent discharge through it. It was then that Sir William Ramsay obtained permission to experiment with the atmospheric nitrogen (*4*), (*40*).

Since these experiments led to such surprising and important results, it may be well to devote a little time to the character and personality of the man who conceived them. William Ramsay's parents were both about forty years old when they married. When, in the following year (October 2, 1852), a son was born to them, the happiness of these good Scotch parents was complete. The child was fond of nature, music, and books, and soon developed a passion for learning new languages. Friends of the family often wondered how the active little fellow could sit so quietly through the long Calvinist sermons at Free St. Matthew's Church in Glasgow. Whenever they looked at him he was intently reading his Bible; but, if they had been close enough, they would have seen that it was never an English Bible, but always a French or German one. The English text was so familiar to him that he rarely needed to consult it, and in this way he gained his first knowledge of these foreign languages (*5*). He also worked out many of his propositions in geometry from the mosaics in the church windows (*6*).

Mr. H. B. Fyfe, one of his classmates at the Glasgow Academy, gave the following account of Ramsay's first chemical experiments:

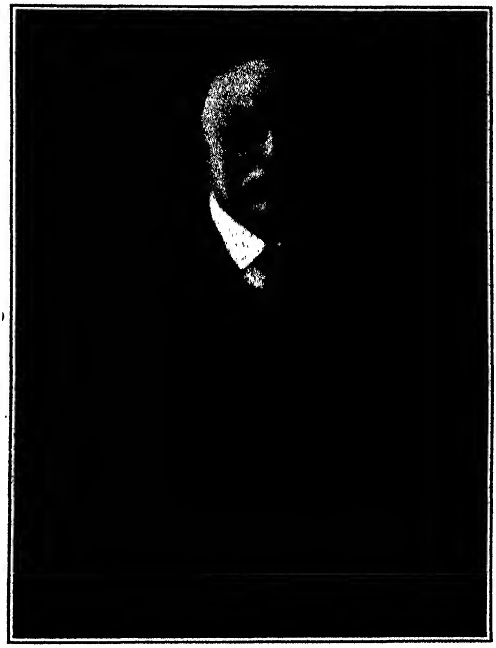
RUDOLF FITTIG, 1835–1910

Professor of organic chemistry at Tübingen and Strasbourg. He discovered the lactones, and devised a general method for synthesizing homologs of benzene. With Erdmann he established the constitution of phenanthrene, and with Remsen he proved the constitution of the alkaloid, piperine. Sir William Ramsay was one of his students.

> At that time he knew nothing of chemistry theoretically, but he had for some time been working at home at various experiments as we called them. He worked in his bedroom, and there were a great many bottles always about, containing acids, salts, mercury, and so on. When we began to meet in this way, I found he was quite familiar with all the ways of getting the material and apparatus for working in chemistry. We used to meet at my house in the afternoons and do what practical work we could, making oxygen and hydrogen and various simple compounds, such as oxalic acid from sugar. We also worked a great deal with glass . . . . We used to work with mouth blowpipes and Bunsen gas burners which we made ourselves, and in this way he became exceedingly expert in working with glass. I think he found this practice very useful in after life. We made nearly all the apparatus we used except flasks, retorts, and beakers. . . (*6*).

William Ramsay always excelled in wholesome amusements such as walking, cycling, rowing, swimming, diving, skating, singing, whistling, and story-telling, and hence had a host of friends. Mr. Fyfe also gave a fine description of Sir William's graceful swimming and diving. "When we were in Paris in 1876," said he, "the four of us used to go to one of the baths in the Seine every forenoon and, after the first time, when Ramsay was ready to dive, the bathman would pass round the word that the Englishman was going to dive and every one in the establishment, including the washerwoman outside, would crowd in and take up positions to watch him" (*6*).

Sir William Ramsay studied at Heidelberg under Bunsen and also at Tübingen under Fittig, and it was at the latter place that he met his lifelong American friend, Ira Remsen (*49*). Although Ramsay later acquired perfect command of the German language, his first words to Remsen sounded like this: "*Können Sie sagen wo ist die Vorlesungszimmer?*" Remsen puzzled over this for a while, and said with a smile, "Oh, I guess you want the lecture room." In later years both Remsen and Ramsay loved to tell this incident, and the former always cherished the honor of having been the first "to open the big front door" for Sir William Ramsay (*7*).



Courtesy Alumni Office, The Johns Hopkins University

IRA REMSEN, 1846–1927

Distinguished American chemist and professor of organic chemistry. President of The Johns Hopkins University. Author of excellent textbooks. Founder and editor of the *American Chemical Journal*. Friend of Sir William Ramsay. He investigated the composition of commercial saccharin.

Argon

After Ramsay had gained permission from Lord Rayleigh to investigate the atmospheric nitrogen, he passed it over red-hot magnesium to find out whether or not it would be completely absorbed. After the gas had been passed back and forth over the hot magnesium, only forty cubic centimeters of it remained, and this residual gas was about $^{15}/_{14}$ as heavy as the original "nitrogen." Professor Ramsay had, of course, taken precautions to exclude dust, water, and carbon dioxide. After prolonged treatment, everything was absorbed except $^{1}/_{80}$ of the original volume. (It will be recalled that Cavendish had obtained a residue amounting to $^{1}/_{120}$ of the original volume (*2*).)

The gas finally obtained had a density of 19.086, and Ramsay and Rayleigh still believed it to be a modification of nitrogen, similar to ozone. However, when Ramsay examined its spectrum, he saw not only the bands of nitrogen but also groups of red and green lines which had never before been observed in the spectrum of any gas. Sir William Crookes made a very thorough study of the spectrum, and observed nearly two hundred lines (*28*).

Rayleigh and Ramsay then worked together, exchanging letters nearly

From Lebon's "Histoire Abrégée de l'Astronomie"

PIERRE-JULES-CÉSAR JANSSEN[*]
1824–1907

French astronomer who directed many astronomical expeditions. Member of the French Institute and of the Bureau of Longitude. In 1868 he observed in the sun's chromosphere a yellow line, D_3, which is now known to belong to the element helium. He was the director of the astrophysical observatory at Meudon.

every day. On May 24, 1894, the latter wrote, "Has it occurred to you that there is room for gaseous elements at the end of the first column of the periodic table?" On August 7, he wrote again, "I think that joint publication would be the best course, and I am much obliged to you for suggesting it, for I feel that a lucky chance has made me able to get *Q* in quantity (there are two other *X*'s, so let us call it *Q* or *Quid?* . . . ." (*8*).

When the British Association met at Oxford in the same month, Ramsay and Rayleigh astonished the members by announcing the discovery of the first inert gas, which, at the suggestion of Mr. H. G. Madan, the chairman, they proposed to call *argon, the lazy one* (*9*), (*25*), (*30*).

Lord Rayleigh died in 1919 (*41*). M. W. Travers said that in all the contemporary correspondence of Sir William Ramsay and Lord Rayleigh which still exists, "there is no indication . . . . of suspicion or sense of injustice on either side" (*40*). Visiting scientists were always surprised at the simplicity of the latter's apparatus. Although the essential instruments were designed and constructed with the utmost skill, the less important parts were assembled with little regard for appearance. His papers were written in a clear, polished style with the mathematical portions in concise, elegant form. His five volumes of collected contributions are prefixed with the motto he himself chose: "The works of the Lord are great, sought out of all them that have pleasure therein" (*41*), (*42*).

Soon after hearing of the discovery of argon, Lecoq de Boisbaudran predicted that it might belong to a family of absolutely inert elements all of which were then unknown, and that their atomic weights[†] would be: 20.0945, 36.40 ± 0.08, 84.01 ± 0.20, and 132.71 ± 0.15. He also predicted that the first two of these elements would be more abundant than the others (*33*), (*34*).

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[*] Reproduced from E. LEBON's "Histoire Abrégée de l'Astronomie" by permission of Gauthier-Villars et Cie., 55 Quai des Grands-Augustins, Paris.

[†] The 1943 atomic weights of the noble gases are: helium, 4.003; neon, 20,183; argon, 39.944; krypton, 83.7; xenon, 131.3; and radon, 222.

Helium

In the year 1868 the French astronomer, Pierre-Jules-César Janssen (*43*), (*44*), went to India to observe a total eclipse of the sun and to make the first spectroscopic study of its chromosphere (*36*). He noticed a yellow line, D_3, which did not quite coincide with the D-line of sodium, and which he could not reproduce in the laboratory. When the English astronomer Sir Norman Lockyer (*22*) found that the new line did not belong to any element then known, he named it *helium* for the sun (*50*), and for a quarter of a century helium was regarded as a hypothetical element which might possibly exist on the sun, but which had never been found on the earth (*10*), (*20*), (*35*). In some of his researches leading up to the discovery of solar helium, Lockyer was assisted by Professor Edward Frankland (*37*).

In 1888–90 the great American mineralogical chemist William F. Hillebrand (*46*) noticed that, when the mineral uraninite is treated with a mineral acid, an inert gas is evolved, which he believed to be nitrogen. When Sir William Ramsay read the paper, he disagreed with this explanation, and repeated the experiment, using, however, another uranium mineral called cleveite (*11*). He obtained a little nitrogen, as Hillebrand had done, but also argon and another gas with different spectral lines. Since he did not have a very good spectroscope, he sent some specimens of the unknown gas to Sir Norman Lockyer and to Sir William Crookes for examination. Lockyer said, "When I received it from him, the glorious yellow effulgence of the capillary, while the current was passing, was a sight to see" (*27*).

FRENCH MEDALLION* CAST IN 1878 IN HONOR OF THE FRENCH ASTRONOMER, JULES JANSSEN, AND THE ENGLISH ASTRONOMER, SIR NORMAN LOCKYER, FOR THEIR METHOD OF ANALYZING THE SOLAR PROTUBERANCES

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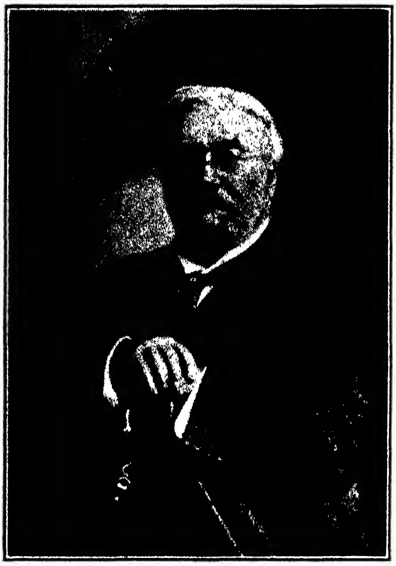

SIR JOSEPH NORMAN LOCKYER*
1836–1920

Director of the solar physics observatory of The Royal College of Science at South Kensington. Pioneer in the spectroscopy of the sun and stars. In 1868 Lockyer and Janssen independently discovered a spectroscopic method of observing the solar prominences in daylight. Such observations had previously been made only at the time of total eclipses of the sun.

On March 17, 1895, Ramsay wrote to Mr. Buchanan, "Crookes thinks its spectrum is new, and I don't see from the method of treatment how it can be anything old, except argon, and that it certainly is not. We are making more of it, and in a few days I hope we shall have collected enough to do a density. I suppose it is the sought-for krypton, an element which should accompany argon. . . ." Before a week had passed, the new gas was shown to be identical with Lockyer's solar element, helium (*21*), (*23*), (*24*), (*26*), (*52*).

On March 24 Sir William wrote to his wife:

> Let's take the biggest piece of news first. I bottled the new gas in a vacuum tube, and arranged so that I could see its spectrum and that of argon in the same spectroscope at the same time. There is argon in the gas; but there was a magnificent yellow line, brilliantly bright, not coincident with, but very close to, the sodium yellow line. I was puzzled, but began to smell a rat. I told Crookes, and on Saturday morning when Harley, Shields, and I were looking at the spectrum in the dark-room, a telegram came from Crookes. He had sent a copy here and I enclose that copy. You may wonder what it means.
>
> Helium is the name given to a line in the solar spectrum, known to belong to an element, but that element has hitherto been unknown on the earth. Krypton was what I called the gas I gave Crookes, knowing the spectrum to point to something new. 587.49 is the wavelength of the brilliant line. It is quite overwhelming and beats argon. I telegraphed to Berthelot at once yesterday: *Gas obtained by me cleveite mixture argon helium. Crookes identifies spectrum. Communicate Academy Monday. . .Ramsay*" (*12*), (*29*).

In the meantime Per Theodor Cleve, the Swedish chemist for whom the mineral cleveite had been named by its discoverer, Nordenskiöld, had his

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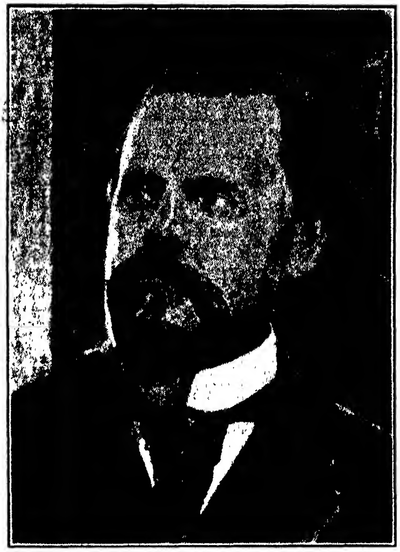
* Reproduced from LOCKYER, T. MARY, AND WINIFRED L. LOCKYER, "The Life and Work of Sir Norman Lockyer," by permission of Macmillan and Co.

student Langlet investigate it (*53*). Although Ramsay announced the discovery before Cleve and Langlet had completed their research, the Swedish chemists were independent discoverers of helium. Langlet's first helium was purer, in fact, than Ramsay's, for he obtained a much better value for its atomic weight (*13*), (*31*), (*32*). The spectroscopic measurements were made by Professor Robert Thalén (*47*).

Immediately after the discovery of argon and helium, Professor Raffaello Nasini of Padua and his collaborators began to search for them in the natural products of Italy, especially in the gaseous emanations. Traveling hour after hour by carriage, on horseback, by mule, or on foot, using portable improvised apparatus in the field, they devoted many years to careful analyses of the natural gases of Italy (*54*). In 1898 they detected helium in the volcanic gases from Monte Irone and in the boric acid soffioni in Tuscany (*55*). It was found only in minute amounts, and in 1897 Clemens Winkler ranked it "among the rarest of elements" (*56*).

In 1903, however, an abundant source of helium was found unexpectedly. During the first half of that year a most unusual gas well was discovered at Dexter, Kansas, and investigated by E. Haworth and D. F. McFarland of the University of Kansas (*57*), (*58*). "It was soon closed in, and an attempt was made to burn it, as natural gas is usually burned, for generating steam for drilling purposes. Much to the surprise of parties interested, it would not burn. Later it was found that when a fire was already kindled in a fire box or an engine and the gas turned on,. . .it would begin to burn and would develop sufficient heat to generate steam moderately well. But as soon as the coal or other fuel in the fire box was consumed, the gas would no longer burn. A cylinder of the gas was shipped to the University of Kansas later during the summer and was partially examined by members of the chemical and geological departments. . . The owners of the well. . . did not wish it given great publicity" (*57*).



PER THEODOR CLEVE, 1840–1905

Professor of chemistry at Upsala. Chairman of the Nobel Committee for chemistry. Cleve and Nils Abraham Langlet, were independent discoverers of terrestrial helium. Sir William Ramsay's announcement was made before their research was completed.

McFarland's analysis of the gas showed the presence of about 15 per cent methane, 72 per cent nitrogen, 12 per cent inert residue, and small amounts of oxygen and hydrogen. Thinking that the inert residue might contain argon or some other inert gas, the late Dr. H. P. Cady and McFarland investigated it further (*59*). Their analysis revealed the presence of 1.84 per cent of helium. On examining many other natural gases from fields in Kansas and elsewhere, they found helium in almost every specimen (*59*).

Courtesy Robert Taft

HAMILTON P. CADY
1874-1943

Codiscoverer with D. F. McFarland of the presence of helium in the natural gases of Kansas; pioneer in research with liquid ammonia. A few years before the close of his life, Dr. Cady perfected an instrument for determining molecular weights rapidly and precisely. *See* ref. (*60*).

Krypton, Neon, and Xenon

Ramsay continued to search for other inert gases, and in this he was aided by his assistant, Morris William Travers. Dr. Travers, who was born in London on January 24, 1872, studied at University College, and received his doctorate in 1893. Soon after this he became intensely interested in Sir William Ramsay's remarkable new elements and in the possibility of discovering another one between helium and argon and two others of higher atomic weight than argon.

Ramsay and Travers tried in vain to find these new gases by heating rare minerals. Their next attempt, and, in fact, their only hope, was to diffuse argon to separate it, if possible, into two fractions of different density. Dr. William Hampson presented them with about a liter of liquid air, which they used, not for liquefying the argon, but for obtaining sufficient skill in manipulation so that they would not risk losing their precious fifteen liters of argon. They were careful, moreover, to save the residues of the liquid air in the hope that these might contain some higher boiling constituents. The residue left after most of the liquid air had boiled away consisted largely of oxygen and nitrogen, which Ramsay and Travers removed with red-hot copper and magnesium (*18*), (*19*).

One day as the younger chemist returned to the laboratory after lunch, a colleague called gaily to him, "It will be the new gas this time, Travers," and with pretended self-confidence he replied, "Of course it will be." Ramsay and Travers then examined the twenty-five cubic centimeters of residual gas, and when they found it to be inert, they immediately placed it in a Plücker tube connected to an induction coil and observed its spectrum. There was a bright yellow line with a greener tint than that of the helium line and a brilliant green line that did not coincide with any line of argon, helium, mercury, or hydrogen (*14*).

They discovered this gas on May 30, 1898, and named it *krypton*, meaning *hidden* (*15*). After working until eleven o'clock that evening on a density determination of the new gas, Ramsay and Travers found that it belonged between bromine and rubidium in the periodic table, and so great was their excitement that the younger chemist almost forgot about his examination for doctor of science which had been scheduled for the next day (*14*).

SIR WILLIAM RAMSAY, 1852–1916

Scottish chemist and physicist who, with Lord Rayleigh and M. W. Travers, discovered the inert gases: helium, neon, argon, krypton, and xenon. He also made a remarkable determination of the atomic weight of radon (radium emanation), the heaviest of the inert gases.

Although krypton was undoubtedly a new element of the zero group, it was not the one for which they had been looking. The gas they had been *expecting* to find would have appeared in the more volatile portion of the argon. Continuing their search for this lighter gas, Professor Ramsay and Dr. Travers liquefied and solidified the argon by surrounding it with liquid air boiling under reduced pressure, allowed the argon to volatilize, and collected the portion that distilled off first. This had a complex spectrum which Ramsay described in his notes as follows: "Lightest fraction of all. This gave magnificent spectrum with many lines in red, a number of faint green, and some in violet. The yellow line is fairly bright, and persists at very high vacuum, even phosphorescence" (*16*).

The vacuum tube containing this most volatile fraction of the argon immediately convinced them that it must be a new gas, for, said Dr. Travers:

> The blaze of crimson light from the tube told its own story, and it was a sight to dwell upon and never to forget. It was worth the struggle of the previous two years; and all the difficulties yet to be overcome before the research was finished. The *undiscovered gas* had come to light in a manner which was no less than dramatic. For the moment, the actual spectrum of the gas did not matter in the least, for nothing in the world gave a glow such as we had seen (*16*).

MORRIS WILLIAM TRAVERS

Honorary professor at the University of Bristol. Formerly director of the Indian Institute of Science in Bangalore. Co-discoverer with Sir William Ramsay of the inert gases, neon, krypton, and xenon. He is an authority on glass technology.

Willie Ramsay, Sir William's thirteen-year-old son, inquired, "What are you going to call the new gas? I should like to call it *novum*." His father liked the suggestion, but thought that the synonymous term, *neon*, would sound better, and it is by this name that the gas discovered in June, 1898, is now known (*16*). In the brilliant neon signs on every business street one may now see at night the "blaze of crimson light" that brought such deep satisfaction and contentment to Professor Ramsay and Dr. Travers.

With the aid of a new liquid-air machine, they prepared larger quantities of krypton and neon, and by repeated fractionation of krypton, a still heavier gas was separated from it, which they named *xenon, the stranger* (*15*). It was discovered on July 12, 1898. Vacuum tubes containing it show forth a beautiful blue glow.

Sir William Ramsay (*48*) had a rare sense of humor. He once said of his visit to the Norwegian chemist, Waage, "He speaks a little German, and with my knowledge of Norse, which as you know is surpassed by few and equalled by none of the natives of that country, we got on very well." In writing of a certain pleasure trip, he said, "I went to Paris with three spirits more wicked than myself, lawyers . . . a fearful compound, 3 lawyers and a chemist . . . just like NCl_3 for all the world, liable to explode at any moment" (*17*).

Sir William was also one of the finest linguists the scientific world ever produced. He could lecture in perfect German before a cultured German audience, or in French before an assembly of French scientists. When presiding in 1913 over the International Association of Chemical Societies, he astonished and delighted his cosmopolitan audience by speaking first in English, then in French, then in German, and occasionally in Italian, always with perfect grace and composure. In spite of his splendid command of languages, his sense of humor sometimes led him to write to members of his family in the following vein: "*Mi Car Dora, . . . Io hab recip vestr litr, ke era mult facil a comprendar . . .*" (*17*).

Ramsay's extended travels never dulled the enthusiasm with which he visited new scenes. Americans may read with pleasure his description of Great Falls, Montana:

> It is a pretty town and perfectly civilized. By the way, in all American towns the electric car is the chief feature. There are overhead wires, and cars like our tram cars run at a prodigious rate, careless of life apparently, yet there are very few accidents. I suppose the fittest, *i. e.*, those who don't get killed, survive. They are delightful as a form of motion and almost rival the bicycle. That creature, too, has penetrated everywhere, and is used even over the prairie (*17*).

Sir William Ramsay's later work on radioactivity is regarded as even more remarkable than his discovery of the inert gases. He died on July 23, 1916, about three years before the death of his distinguished collaborator, Lord Rayleigh.

Dr. Travers served from 1906 to 1914 as director of the Indian Institute of Science in Bangalore, and in 1921 he became president of the Society of Glass Technology (*51*). He is an honorary professor at the University of Bristol. In 1928 he wrote a book entitled "The Discovery of the Rare Gases," which is illustrated with pictures of apparatus and facsimile pages from Sir William Ramsay's notebooks (*9*).

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XXVI. THE NATURAL RADIOACTIVE ELEMENTS

In 1898 there was discovered an element, radium, which continually and spontaneously emits light, heat, and other radiations. Investigation of these astonishing phenomena by the Curies and many others has revealed about forty interrelated radioactive elements which, like radium, are unstable. They do not, however, occupy forty places in the periodic system, but are crowded into only ten places. The explanation for the existence of these numerous so-called "radioactive isotopes" and their genealogical descent from uranium and thorium were discovered independently by K. Fajans, F. Soddy, A. S. Russell, and A. Fleck. Since the original literature on the radioactive elements embraces such a vast field of research, the following account of their discovery is necessarily far from complete.

. . . . . .

> "*Radium is not to enrich any one. It is an element; it is for all people*" (*1*).
>
> "*So the atoms in turn, we now clearly discern,*
> *Fly to bits with the utmost facility;*
> *They wend on their way, and, in splitting, display*
> *An absolute lack of stability*" (*2*).

Henri Becquerel, a member of a family renowned for scientific achievement, noticed in 1896 that when a phosphorescent salt, such as potassium uranyl sulfate, is placed near a photographic plate protected by black paper, the plate becomes fogged as though it had been exposed to light (*51*), (*58*). His later work showed that all uranium compounds, even those which do not phosphoresce, give off penetrating rays which, like X-rays, darken a photographic plate and, by making the surrounding air a conductor, cause the gold leaves of a charged electroscope to lose their electrostatic charge and collapse. These radiations are now known to be of three kinds: alpha rays, which consist of helium atoms each bearing two units of positive electricity; beta rays consisting of streams of negative electrons; and gamma rays, which constitute a very penetrating radiation of extremely short wave-length.

PIERRE CURIE, 1859–1906

Professor of physics at the Sorbonne. In collaboration with his brother, Jacques Curie, he discovered and investigated piezo-electricity. He introduced the concept of symmetry in physical phenomena, studied magnetic properties as a function of temperature, and collaborated with Mme. Curie in discovering radium and investigating its properties.

The amazingly rapid development of the science of radioactivity is largely due to the brilliant work of M. Pierre Curie and his wife, Mme. Marie Sklodowska Curie. The former was born in Paris on May 15, 1859, and was educated by his cultured parents. Many happy hours were spent on excursions to the country, and thus this city child grew up in intimate contact with nature, collecting plants and animals and enjoying them in quiet contemplation. While serving as director of the laboratory under Schützenberger at the School of Physics and Chemistry, Pierre Curie carried on researches on condensers, magnetism, piezo-electricity, and the principle of symmetry in nature. When in 1895 he received the degree of *Docteur-ès-sciences* from the Sorbonne, Schützenberger created a chair of physics for him (*3*).

Marie Sklodowska, a daughter of Dr. Sklodowski,* a professor of physics and mathematics at the Warsaw gymnasium, was born on November 7, 1867. Because of the early death of her gifted mother, the little girl grew up in her father's laboratory and under his instruction. She soon developed a passionate love of country and joined a secret society of students who organized evening classes for laborers and peasants. However, because of the limited opportunities for advanced study, she decided to leave her beloved motherland and go to Paris (*99*).

ANTOINE-HENRI BECQUEREL
1852–1908

French physicist and engineer. Discoverer of the rays emitted by uranium. He carried out important researches on rotatory magnetic polarization, phosphorescence, infra-red spectra, and radioactivity. His grandfather Antoine-César-Becquerel (1788–1878), and his father, Alexandre-Edmond Becquerel (1820–91), also made many important contributions to chemistry and physics.

During the four years of her student life, she lived in a chilly little attic room, carrying the coal herself up the six flights of stairs, and cooking her simple meals over an alcohol lamp. This was Marie Sklodowska's introduction to the city which became her permanent home (*4*), (*68*). When she enrolled at the Sorbonne, Henri Poincaré, the famous mathematical physicist, soon recognized her ability, and Professor Gabriel Lippmann also took great interest in her research.

Her first meeting with Pierre Curie was at the home of a Polish physicist in Paris. Because of their mutual interest in scientific, social, and humani-

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* The feminine ends in *-ska*, the masculine in *-ski*.

tarian subjects, there gradually developed a singleness of purpose that caused M. Curie to say, "It would . . . be a beautiful thing in which I hardly dare believe, to pass through life together hypnotized in our dreams: your dream for your country; our dream for humanity; our dream for science." After their marriage in 1895 Professor Schützenberger arranged that they might work together in the laboratory, and their mutual devotion to science once led M. Curie to remark, "I have got a wife made expressly for me to share all my preoccupations" (*5*).

Polonium and Radium

Professor Curie continued his researches on the growth of crystals, and his young wife prepared for her examinations. Many chemists consider her dissertation (*55*) to be the most remarkable thesis ever presented for the doctorate. She continued the work begun by Becquerel, and tested most of the known elements, including a number of rare ones loaned by Demarçay and Urbain, with Prof. Curie's piezo-electric quartz electrometer, and found that thorium and uranium were the only ones whose compounds produced appreciable ionization (*26*), (*54*), (*55*). The radioactivity of thorium was discovered independently by Gerhardt Carl Schmidt, professor of physics at the University of Münster (*25*).

(JULES) HENRI POINCARÉ, 1854–1912
French mathematician, physicist, and astronomer. Prolific and gifted writer on mathematical analysis, analytical and celestial mechanics, mathematical physics, and philosophy of science.

GABRIEL LIPPMANN, 1845–1921
Professor of mathematical physics at the University of Paris. Inventor of the capillary electrometer and of a process of direct color photography. The phenomenon of piezo-electricity in crystals predicted by Professor Lippmann was first demonstrated experimentally by Pierre and Jacques Curie.

THE LABORATORY[*] IN WHICH M. AND MME. CURIE DISCOVERED RADIUM

Of much greater significance than this, however, was Mme. Curie's observation that the activity of the uranium mineral, pitchblende, is four or five times as great as one might expect it to be from its uranium content (*24*). She concluded that the ore must contain another radioactive element in addition to uranium, and that, since the composition of the ore was known, the active element must be present in extremely small amount and must therefore be very active indeed. Therefore it became necessary to work up large quantities of pitchblende and to make elaborate and tedious fractionations of this complex ore. The pitchblende was supplied by the Austrian government from its uranium mines in the Joachimsthal, Bohemia.

As Mme. Curie examined each fraction with the electrometer, she found that a very active substance separated with the bismuth. After convincing herself in 1898 that this was a new element, she named it *polonium* in honor of her native country (*27*), (*65*). It is also known as *radium F*. In 1902 Dr. Willy Marckwald of Berlin obtained a metallic deposit on a polished plate of bismuth immersed in a solution of the bismuth fraction from pitchblende. This deposit, which he called radiotellurium, was later shown to be identical with Mme. Curie's polonium (*6*), (*29*).

After commenting on the discovery of gallium, scandium, and germanium (eka-aluminum, eka-boron, and eka-silicon), Mendeléeff had written in 1891, "I foresee some more new elements, but not with the same certitude as before. I shall give one example, and yet I do not see it quite distinctly" (*7*). He had then proceeded to describe an undiscovered "dvi tellurium"

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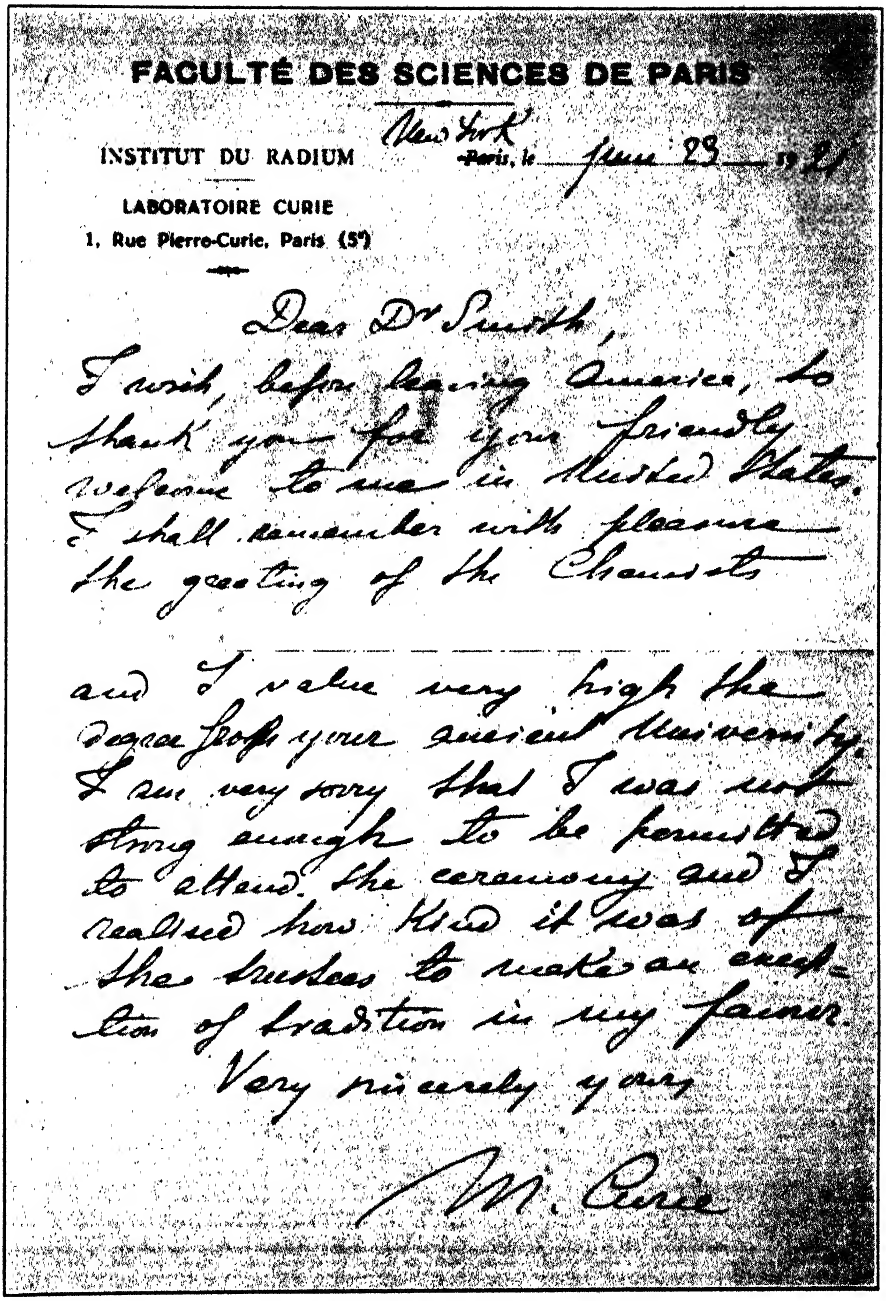
[*] Reproduced from an article by JACQUES DANNE, *La Nature*, **32**, [1], 217 (Mar. 5 1904) by permission of Masson et Cie., Paris.

From Z. Elektrochemie,
Courtesy Verlag Chemie

Left to Right:

Back row: G. v. Hevesy, H. Geiger, J. Chadwick, K Przibram, F. Paneth
Front row: O. Hahn, Lord Rutherford, Lise Meitner, Stefan Meyer



FACULTÉ DES SCIENCES DE PARIS

INSTITUT DU RADIUM

LABORATOIRE CURIE

1, Rue Pierre-Curie, Paris (5e)

New York ~~Paris~~, le June 23 1921

Dear Dr Smith,

I wish, before leaving America, to thank you for your friendly welcome to me in United States. I shall remember with pleasure the greeting of the Chemists

and I value very high the degree from your ancient University. I am very sorry that I was not strong enough to be permitted to attend the ceremony and I realised how kind it was of the trustees to make an exception of tradition in my favour.

Very sincerely yours

M. Curie

Edgar Fahs Smith Memorial Collection, University of Pennsylvania

AUTOGRAPH LETTER FROM MME. CURIE TO DR. EDGAR F. SMITH with an atomic weight of about 212. Since polonium resembles tellurium and has an estimated atomic weight of about 210, it is probably the realization of Mendeléeff's "dvi tellurium."

MME. MARIE SKLODOWSKA CURIE
1867–1934

Professor of radioactivity at the University of Paris. With her husband, Professor Pierre Curie, she discovered radium and polonium, and founded the science of radioactivity.

After the Curies, with the assistance of M. G. Bemont, had carried out many laborious fractionations of barium chloride, they found that the most insoluble fractions were the most radioactive. In the course of her experiments Mme. Curie had learned that radioactivity is an atomic property depending solely on the quantity of active element present. For this reason the presence of another active element was suspected, and the radioactive barium chloride was therefore submitted to M. Demarçay for spectroscopic examination. He detected a new line in the ultra-violet region of the spectrum, and certain other lines, all of which were most distinct in the most radioactive preparations, and, as fractionation proceeded, the barium lines became fainter and fainter (*23*), (*28*), (*52*).

While tracing down the new element, the Curies often wondered how its salts would look, and hoped that perhaps they might display beautiful colors. The radium chloride which they finally obtained proved to be a white salt, however, but it was even more beautiful than their brightest dreams: it glowed in the dark! Radium, like phosphorus, is a giver of light, and this property was to them, as it had been to Brand and Kunckel, a source of surprise and delight. "One of our joys," writes Mme. Curie, "was to go into our workroom at night; we then perceived on all sides the feebly luminous silhouettes of the bottles or capsules containing our products. It was really a lovely sight and always new to us. The glowing tubes looked like faint fairy lights" (*8*), (*60*).

The new substance was named *radium*, the giver of rays, and, were it not for this property, it might still be numbered among the missing elements. Although it gives a distinct spectrum, the method of detecting it with an electrometer is five hundred thousand times more sensitive than the spectroscopic method (*9*).

The late Professor Georges Urbain once said:

> I was certainly privileged, for I saw with my own eyes the birth of radium. Pierre Curie, who was my teacher, rendered me the incomparable honor of according me his confidence and friendship. I saw Mme. Curie work like a man at the difficult treatments of great quantities of pitchblende. I saw the first fractionations of the bromides of barium-radium. I saw the radium-bearing crystals shine in the dark before the radium spectrum could be observed in them. Every Sunday we used to go with Langevin, Perrin, Debierne, Cotton, and Sagnac to the little Curie home, which was thus transformed into an intimate academy. There the master, with his customary simplicity, explained his ideas to us and deigned to discuss ours. . . (*74*).

The late Wilhelm Ostwald gave in his autobiography the following account of his visit to the birthplace of radium:

> At my urgent request the Curie laboratory, in which radium was discovered a short time ago, was shown to me. The Curies themselves were traveling. It was a cross between a horse-stable and a potato-cellar, and, if I had not seen the worktable with the chemical apparatus, I would have thought it a practical joke (*10*).

When M. Curie was offered the decoration of the Legion of Honor, he wrote, "I pray you to thank the Minister, and to inform him that I do not in the least feel the need of a decoration, but that I do feel the greatest need for a laboratory." Nevertheless, Mme. Curie regarded the years spent in this dingy old shed as "the best and happiest" of her life (*8*).

The Uranium Series

In 1900 Sir William Crookes prepared a solution containing a uranium salt and a small amount of a ferric salt. When he added to this an excess of a solution containing ammonium hydroxide and ammonium carbonate, he found that the resulting ferric hydroxide precipitate was intensely radioactive. After studying the radioactive properties of the substance which precipitates with the iron, he said, "For the sake of lucidity the new body must have a name. Until it is more tractable I will call it provisionally UrX—the unknown substance in uranium" (*30*). It is now known as *uranium* X_1. McCoy and Ross, Boltwood, and R. B. Moore and H. Schlundt found independently that there are two uraniums, ***uranium 1*** and *uranium 2* (*12*), (*48*), (*81*), (*108*), (*109*), (*110*).

In 1913 Kasimir Fajans and O. H. Göhring of Karlsruhe showed that uranium X_1 disintegrates by β-ray emission into a very short-lived product which they called ***brevium*** (*11*), (*48*), but which is now known as ***uranium*** X_2. Professor Fajans taught physical chemistry for many years at the University of Munich and is now teaching at the University of Michigan (*70*). Like Mme. Curie he is a native of Warsaw. Mendeléeff predicted the discovery of uranium X_2 in 1871 when he said, "There is a third vacant place at series 12 in group V between Th = 231 and U = 240 for an element which forms [the oxide] R_2O_5 and has an atomic weight of about 235" (*71*).

Since uranium X_1 gives two kinds of β-rays, it yields two radioactive products: *uranium X_2* and *uranium Z* (*12*). The latter substance, which was discovered by Professor Otto Hahn in 1921, is a subordinate branch of the family, however, for the disintegration of uranium X_1 yields 99.65 per cent of uranium X_2 and only 0.35 per cent of uranium Z.

Professor Hahn is a native of Frankfort-on-the-Main. He collaborated with Sir William Ramsay, and later with Miss Lise Meitner. He is a member of the German Atomic Weight Commission and director of the Kaiser Wilhelm Institute for Chemistry in Berlin-Dahlem. Miss Meitner, who was also on the staff of this Institute, is a native of Vienna.

Courtesy Cornell University

KASIMIR FAJANS, 1887–

American physical chemist, born in Poland. Professor at the University of Michigan. Codiscoverer with Göhring of uranium X_2 (brevium). In 1913 he discovered, simultaneously with Soddy, the law of radioactive displacement of elements in the periodic system as the result of α- and β-ray emission.

There is also a sixth member of this series, known as *uranium Y* (*46*), (*50*), (*56*), (*59*), which was discovered in 1911 by G. N. Antonoff, who was working under Sir Ernest Rutherford at the University of Manchester. He afterward returned to St. Petersburg. Uranium Y, like uranium Z, belongs to a subordinate branch of the family. Soddy attributed Antonoff's success, not to the special chemical process adopted, but "to the lapse of a suitable period of time between successive separations" (*75*). Thus in the uranium series uranium 1 breaks down to form uranium X_1, and this in turn disintegrates to form the successive products: uranium X_2, uranium Z, uranium 2, and uranium Y.

The Radium Series

In 1904 B. B. Boltwood, H. N. McCoy, and R. J. Strutt proved independently that radium is produced by spontaneous transmutation of uranium (*107*). Three years later Boltwood discovered an element which he named *ionium* and which he found to be the parent substance of radium (*39*). Professor Boltwood had acquired a broad cosmopolitan education in Munich, Leipzig, Manchester, and New Haven, and was a skilled laboratory technician, a sympathetic teacher, and a polished gentleman with "a certain courtliness of manner." He proved that there is a genetic relationship between uranium, ionium, and radium (*13*). Ionium was discovered independently at about the same time by Hahn and by Marckwald (*14*), (*73*), (*77*).

The second member of the series is radium itself. The task of isolating it was most difficult, and involved risk of losing the precious product. In 1910, however, Mme. Curie and M. Debierne finally succeeded in preparing the shining white metal; but, since they needed the radium in their researches, they did not keep it in this form.

The Edgar F. Smith Memorial Collection, University of Pennsylvania

BERTRAM BORDEN BOLTWOOD
1870–1927

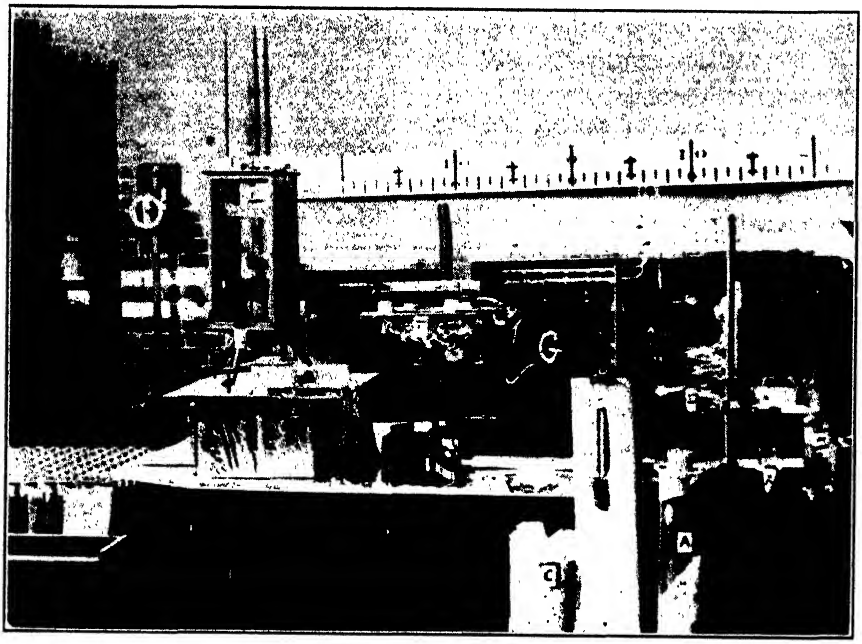
Professor of chemistry and physics at Yale University. Discoverer of the radioactive element ionium, the parent of radium. Ionium was discovered independently at about the same time by Hahn and by Marckwald.

Photo by William Notman & Son, Ltd.

HARRIET BROOKS, 1876–1933
(MRS. FRANK PITCHER)

In 1902 Rutherford and Miss Brooks studied the penetrating power of α-rays from various sources and made the first attempt to determine the density of radon by a diffusion method. Their study led to the discovery of radium A, B, and C. This photograph was taken in 1898 when Miss Brooks obtained her B.A., McGill University.

Like all radioactive elements, it undergoes continuous, spontaneous disintegration into elements of lower atomic weight. M. and Mme. Curie had noticed that when air comes in contact with radium compounds it, too, becomes radioactive. The correct explanation was first given in 1900 by Friedrich Ernst Dorn, who was born on July 27, 1848, at Guttstadt in eastern Prussia. He studied at Königsberg and taught physics for many years at Darmstadt and at Halle. Professor Dorn showed that



Condensation of the Radium Emanation on the Occasion of Professor Cox's Lecture on Liquid Air in the Macdonald Physics Building at McGill University, Nov. 6, 1902

The original coil of Rutherford and Soddy which appears in this picture and in which the first condensation was effected is still in the Physics Building at McGill University. The original photograph bears the initials F. S. [Soddy].* It was in the Macdonald Physics Building that Rutherford and Soddy proved that the radioactive elements undergo spontaneous transformation.

one of the disintegration products of radium is a gas (*15*), (*37*). This was at first called ***radium emanation***, or ***niton***, but, since it is derived from radium, the modern name ***radon*** is to be preferred. After showing that the highest temperatures obtainable had no effect on the rate of transformation of this emanation, Rutherford and Soddy decided to try the effect of extreme cold. According to Professor A. S. Eve, "Within a quarter of an hour after the first 100 cc. of liquid air were prepared, the emanation had been condensed, and the material nature of this gas had been proved beyond question" (*103*). It is the last member of the group of noble gases previously discovered by Sir William Ramsay (*62*), and in 1910 the remarkable density determination of Ramsay and Robert Whytlaw Gray proved that it is the heaviest gas known (*91*).

In 1904 Miss Harriet Brooks of McGill University in Montreal studied

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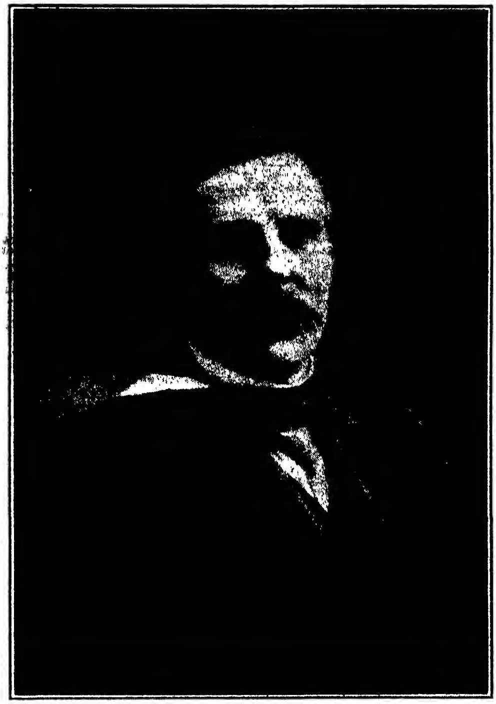
* The writer wishes to thank Dr. William H. Barnes and Dr. A. S. Eve of McGill University for their kind assistance in procuring the photograph of the apparatus for condensing radon and the portraits of Miss Brooks (Mrs. Pitcher) (p. 493) and Professor Owens (p. 502).

the "active deposit of short life" which forms as a thin layer on all substances which have been exposed to radon (*43*), a phenomenon which Soddy has compared to "a sort of continuous snowstorm silently going on covering every available surface with this invisible, unweighable, but intensely radioactive deposit" (*83*). From Miss Brooks's researches and his own, Rutherford concluded that radon forms three successive disintegration products: radium A, B, and C. These were found and separated, and in "the active deposit of long life" there were discovered three additional elements: radium D, E, and F (polonium), which are products of further disintegration (*11*), (*53*).

Sir Ernest Rutherford was born in 1871 in Nelson, New Zealand. After studying at New Zealand University and Cambridge, he went to Canada in 1898 as a professor of physics at McGill University. After serving there for nine years and carrying out many remarkable researches in radioactivity, he became professor of physics at Manchester University, and in the following year he was awarded the Nobel Prize in chemistry. In 1919 he became a professor at Cambridge (*72*).



Courtesy Mr. Sederholm, Nobelstiftelsen, Stockholm

LORD RUTHERFORD, 1871–1937

Professor of physics at McGill, Manchester, and Cambridge Universities. He identified the three types of radiations from radioactive substances, and devised methods for counting alpha particles and for determining the number of free positive electrons in the nucleus of an atom.

His three greatest discoveries were the proof of the transmutation of radium into other elements (Rutherford and Soddy), the nuclear atom, and artificial transmutation. Lord Rutherford took his teaching duties very seriously and was exceedingly kind to his students and collaborators and most generous in sharing with them his ideas and his honors. Because of his remarkable genius for planning research and apportioning to every worker a task suited to his ability, he trained many of the physicists and chemists who are now working in the great research institutes throughout the world (*104*).

Professor H. Geiger states that Lord Rutherford "threatened the severest penalties" for anyone who allowed emanation to escape, for it spread rapidly throughout the building and made it impossible to work with the electroscope. One day when Geiger's counting experiments were thus interrupted, he found that the emanation was coming from the room where Rutherford was working. When informed of the trouble, Rutherford replied, "Well, there you have further proof of the power inherent in this emanation." Thereupon he took Dr. Geiger for a ride in the country and "was soon discoursing on his own experiments and on all the problems that were yet to be solved. Nothing was so refreshing nor so inspiring as to spend an hour in this way, alone with Rutherford" (*102*).

According to J. J. Thomson, Lord Rutherford's death on October 19, 1937, "just on the eve of his having in the High-Tension Laboratory means of research far more powerful than those with which he had already obtained results of profound importance, is, I think, one of the greatest tragedies in the history of Science" (*101*), (*102*). Lord Rutherford was the first scientist born in the overseas dominions to be buried in Westminster Abbey, beside the graves of Newton, Kelvin, Charles Darwin, and Sir John Herschel.

Hahn and Meitner (*82*) and Fajans (*33*) found that radium C disintegrates in two ways, forming radium C′ and radium C″. K. A. Hofmann and Eduard Strauss noticed in 1900 that radium D has a strong resemblance to lead, and these two elements were later found to be inseparable (*38*). Karl A. Hofmann was associated with Adolf Baeyer at Munich.

Elster and Geitel also made pioneer researches on "radio-lead," of which radium D is the principal constituent (*42*).

Julius Elster was born on December 24, 1854, at Blankenburg, Germany (*85*), and studied at Berlin and Heidelberg. In 1881 he began his teaching career at the Wolfenbüttel Gymnasium, where he was destined to serve for nearly forty years and to carry out many brilliant researches with his intimate friend, Hans F. K. Geitel (1855–1923). They showed that the radioactivity of common lead is not a specific property of the element, but that it is always caused by admixture of some radioactive substance. Very old specimens of lead, which no longer contain radium D, are inactive (*85*). The friendship of Elster and Geitel lasted from childhood throughout life. During their first years at Wolfenbüttel, they lived with Geitel's mother. After her death, Elster married, and built a fine, hospitable home and private laboratory, where Geitel became a permanent member of the household and where they prepared more than a hundred joint papers. Together they proved that the electrical conductivity of the atmosphere is not caused by dust but by ions produced by radioactive substances present in the air. They also demonstrated the surprisingly wide distribution of radioactive substances. Simultaneously with Sir William Crookes, they observed the scintillations of Sidot blende when bombarded with alpha particles. As early as 1899 they recognized that the atom of a radioactive element is unstable and that it gradually breaks down into the stable atom of an inactive element. Since Elster and Geitel were of almost the same age and since their names are inseparable, German physicists chose an intermediate date for the observance of their sixtieth birthday (*96*), (*106*). Professor Elster died at Wolfenbüttel on April 8, 1920 (*96*).

Ramsay, Soddy, Fajans, and Georg Bredig were all greatly interested in the anomalous atomic weights of lead from various sources, and Fajans sent his assistant, Max E. Lembert, to America to work on this problem with the late Theodore William Richards at Harvard (*67*), (*78*). Fajans also provided Professor Richards with several radioactive ores containing lead. After studying ores from Ceylon, Colorado, England, Norway, and Bohemia, Richards and Lembert announced in 1914 that the atomic weight of lead from such minerals is much lower than 207.2, the value accepted for ordinary lead (*16*), (*78*), (*87*). O. Hönigschmid and Mlle. Stephanie Horovitz (*79*) of Vienna and Maurice Curie (*92*) made the same discovery independently at about the same time.

These two kinds of lead are now known to be *isotopes*, or inseparable elements which belong in the same space in the periodic table and yet differ in atomic weight and in radioactive properties. According to Frederick Soddy, the first clear recognition of isotopes as chemically inseparable substances was that of H. N. McCoy and W. H. Ross in 1907 (*75*), (*107*). Strictly speaking, the science of radioactivity has revealed only five naturally occurring new elements with distinctive physical and chemical properties: polonium, thoron, radium, actinium, and uranium X_2. All the other natural "radioactive elements" share previously occupied places in the periodic table.

Since the activity of polonium in time disappears completely, and since the ratio of lead to uranium is almost constant in all primary uranium minerals from a given geological formation, the last stage in the disintegration of uranium is believed to be a stable element, *uraniolead*, or *radium G*, which is inseparable from ordinary lead. The members of the radium series are: ionium, radium, radon, and radium A, B, C, C′, C″, D, E, F, and G.

The Actinium Series

Protoactinium, the patriarch of the actinium series of elements, was discovered in 1917 by Otto Hahn and Miss Lise Meitner and independently by Frederick Soddy and John A. Cranston at about the same time (*47*), (*49*), (*50*). In 1927, Dr. Aristid V. Grosse* succeeded in preparing two milligrams of a white powder which was shown to be the pentoxide

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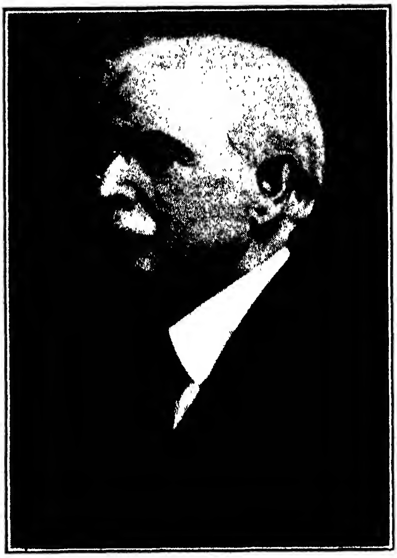
* The process patented by Grosse and Hahn for preparing pure Pa_2O_5 is described in *Chem. Zentr.*, 102, 3525–6 (1931).



Courtesy Harvard University

THEODORE WILLIAM RICHARDS
1868–1928

Director of the Wolcott Gibbs Memorial Laboratory at Harvard University. The precision of his atomic weight determinations has never been surpassed. He discovered the anomalous atomic weights of lead from radioactive minerals.

DR. JOHN A. CRANSTON

Member of the Council of the Society of Chemical Industry. Chairman of the Glasgow Section. He has collaborated with Frederick Soddy in important researches on radioactivity, and is an independent discoverer of the element protoactinium, Mendeléeff's predicted eka-tantalum.

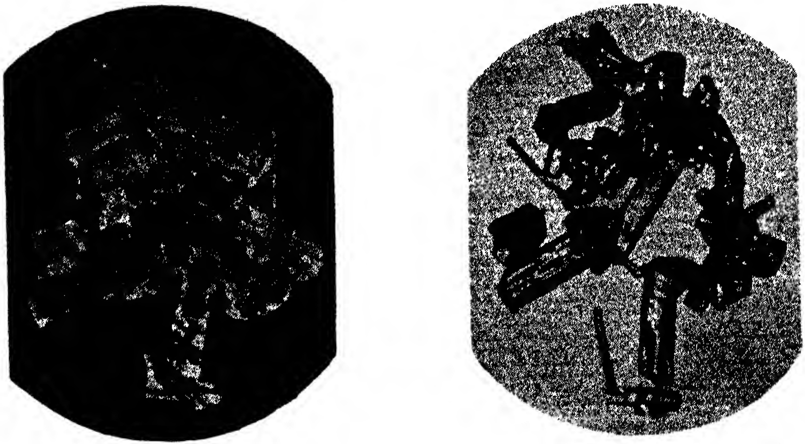
of protoactinium, Pa_2O_5 (*88*). Grosse and Agruss later worked up large quantities of radium residues from Joachimsthal, Czechoslovakia (now Sudeten-Germany), at the Lindsay Light Company. The residues were extracted with hydrochloric acid, and the siliceous residue containing the protoactinium was fused with sodium hydroxide. After leaching the basic oxides from the melt, Grosse and Agruss precipitated zirconium phosphate, which carried down with it the protoactinium. They succeeded in concentrating the protoactinium from the original value of about 0.3 gram per metric ton in the Joachimsthal residues to 1 part per 1000 in the plant product, which they further concentrated in the laboratory by fractional crystallizations of zirconium oxychloride and repeated precipitation of zirconium phosphate. Most of the zirconium was finally separated by sublimation of the chlorides, after which the protoactinium was precipitated with hydrogen peroxide. In this way they isolated 0.1 gram of pure protoactinium pentoxide (*95*).

In the fall of 1934, Dr. Grosse reduced this pure oxide by two methods and obtained from it the metal protoactinium, which is even rarer than radium, but much more permanent in air. In the first method, he bombarded the oxide on a copper target, in a high vacuum, with a stream of electrons. After a few hours, he obtained "a shiny, partly sintered, metallic mass, stable in air." In his second method, he converted the oxide to the iodide (or chloride or bromide) and "cracked" it in a high vacuum on an electrically heated tungsten filament, according to the reaction:

$$2PaI_5 = 2Pa + 5I_2$$

The metallic protoactinium retained its bright luster for some time (*95*).

Dr. Grosse then converted part of his pure protoactinium pentoxide into potassium protoactinium fluoride, K_2PaF_7, which can easily be dried to constant weight. Using the classical method which Marignac had used for determining the atomic weight of tantalum, he weighed the new element both as the pentoxide and as potassium protoactinium fluoride. His duplicate results for the atomic weight of protoactinium, made on this very small sample but with precise technique and apparatus, are 230.4 and 230.8.* These researches are especially important because they will probably lead to a much better understanding of the entire actinium series. Protoactinium is an isotope of uranium Z and of uranium X_2, and thus there are at least three radioactive elements all identical in chemical and physical properties with Mendeléeff's predicted eka-tantalum (*17*).



Proc. Roy. Soc. (London)

CRYSTALS OF POTASSIUM PROTOACTINIUM FLUORIDE—K_2PaF_7

(Left: Dark field illumination; × 60.)

In 1899 André Debierne, a young chemist who had served as *préparateur* under Friedel and who was an intimate friend of the Curie family, discovered that another radioactive element is carried down with the precipitate of the rare earths produced by adding ammonium hydroxide to a

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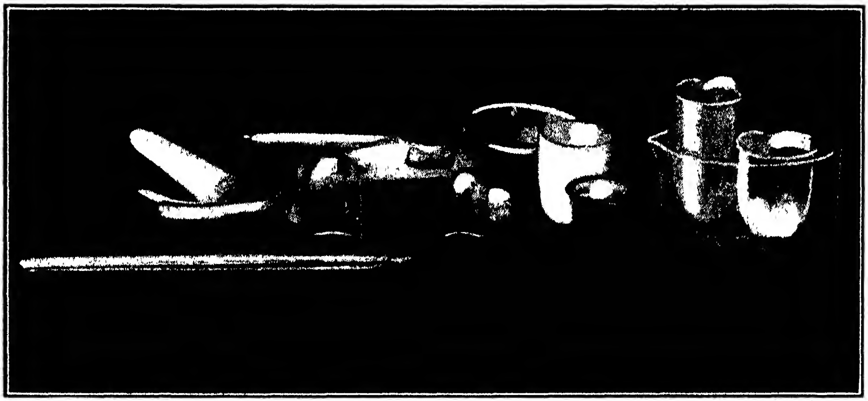
* The 1943 atomic weight of protoactinium is 231.

solution obtained by dissolving pitchblende(*40*). This element, which he named actinium, was discovered independently in 1902 by F. Giesel, who removed it with the lanthanum and cerium (*41*) and called it *emanium*.

The actinium series is very much like that of radium. In 1904 and 1905 Giesel and T. Godlewski, while working independently, discovered the element actinium X, which is precipitated with the ferric hydroxide by adding an excess of ammonium carbonate solution to a solution containing actinium and iron (*41*), (*44*).

Friedrich O. Giesel (1852–) was for many years a chemist at the quinine works of Braunschweig Buchler and Company, and in the early days he worked up large quantities of radioactive minerals and generously distributed his radium among investigators in all parts of the world (*56*).

Tadeusz Godlewski, the youngest son of Emil Godlewski, the famous plant physiologist, was born on January 4, 1878, at Lemberg, Poland. After graduating from the ancient Jagellonian University at Cracow, he went to Stockholm for a year of graduate study under Arrhenius. A year of research under Sir Ernest Rutherford at Montreal resulted in the publication of three papers on radioactivity. After returning to Poland, he became professor of physics and rector at the Technische Hochschule of Lemberg, where he continued his original investigations in radioactivity and electrochemistry. His life was all too short, and it is believed that his death in 1921 was caused by leakage of coal gas in his laboratory (*89*).



Courtesy Scientific American

APPARATUS USED BY DR. ARISTID V. GROSSE IN HIS RESEARCHES ON PROTOACTINIUM
This diminutive apparatus occupies a total length from left to right of about eleven centimeters.

In 1906 Professor Hahn discovered radioactinium between actinium and actinium X (*45*). Actinium emanation, or *actinon*, which, like radon, is an inert gas, was discovered independently by F. Giesel and André Debierne (*40*), (*41*). The other members of the series, actinium A, B, C, C′, C″, and D, are analogous to the corresponding members in the radium series (*43*), (*64*). It was proved by Boltwood that there is a genetic relationship between the uranium, the radium, and the actinium series of elements, and in 1915 F. Soddy and Miss A. F. Hitchins measured the steady growth of radium in purified uranium preparations (*39*), (*57*).

The Thorium Series

The thorium series is apparently independent of the three just named. In 1905 Otto Hahn, working under Sir William Ramsay's direction, discovered *radiothorium* in the residues from a Ceylon mineral called thorianite, and two years later he showed that *mesothorium* is an intermediate disintegration product (*19*), (*35*), (*36*).

ALEXANDER SMITH RUSSELL

Scottish chemist who discovered the effect of a beta-ray change on the atomic number of an element. Lecturer on inorganic chemistry at Oxford University. He has carried on chemical research, especially in radioactivity, in the laboratories of Soddy in Glasgow, of Nernst in Berlin, and of Rutherford in Manchester. His publications include many research papers, literary contributions, and a book on the chemistry of radioactive substances.

ALEXANDER FLECK

Author of many research papers on the radioactive isotopes. He proved the inseparability of uranium X_1 and radioactinium from thorium, of thorium B and actinium B from lead, of mesothorium 2 from actinium, of radium E from bismuth, and of radium A from polonium, and confirmed the discovery of uranium X_2 by Fajans and Göhring. He is now connected with the Imperial Chemical Industries, Ltd.

Since the radioactivity of thorium salts is smaller than that of the minerals, B. B. Boltwood (*93*) thought that some of the radiothorium must have been lost during the purification process. On the assumption that radiothorium was formed directly from thorium, he computed that the half-life period of the former ought to be at least six years, whereas Hahn obtained an experimental value of only two years. Hahn therefore assumed that there must exist between thorium and radiothorium an unknown rayless product, *mesothorium*, which can easily be separated from thorium in the purification process.

He found that freshly prepared thorium salts have a normal radioactivity which decreases to a minimum in 4.6 years. He computed that the undiscovered member ought to have a half-life period of five and one-half years, and two chemists at the University of Chicago, Herbert N. McCoy (*100*) and William H. Ross, later verified this prediction. The new element was at first called *mesothorium*, but is now known as *mesothorium 1* (*20*), (*63*), the name having been changed because Hahn afterward found

Photo by William Notman & Son, Ltd.

R. B. OWENS

He observed in 1899 that the ionization current through a confined volume of air exposed to the rays from thorium compounds decreased to a minimum when air was drawn through his apparatus. Rutherford showed that this effect is caused by the emission of thorium emanation, now known as thoron. This photograph was taken in about 1910 when Professor Owens was at McGill University.

Courtesy Ralph E. Oesper

FREDERICK SODDY, 1877–

Professor of chemistry at Glasgow, Aberdeen, and Oxford. Author of books on radioactivity and economics. He showed that when a radioactive element emits alpha particles, its position in the periodic table is shifted two spaces to the left, whereas a beta-ray change causes a shift of one space toward the right. This rule, which explains the existence of radioactive isotopes, was discovered independently by A. S. Russell, A. Fleck, Soddy, and Fajans.

that mesothorium 1 disintegrates into a short-lived product, *mesothorium 2*. Soddy's brilliant elucidation of the chemistry of mesothorium 1 led to his theory of radioactive isotopes, for which he was awarded the Nobel Prize (*66*).

Because of its lower cost, mesothorium 1 is frequently substituted for radium in therapy and in the manufacture of luminous watch-dials. The commercial process for extracting it from the by-products of monazite sand was long kept secret, but after Soddy and Marckwald independently discovered that it is chemically identical with radium, the process for extracting the latter element from pitchblende was adapted so that it could be used for recovering mesothorium 1 (*84*), (*94*).

In 1902 Rutherford and Soddy added ammonium hydroxide to a thorium solution, filtered off the thorium hydroxide precipitate, and found that, after evaporating the thorium-free filtrate to dryness and fuming off the ammonium salts, the residue was much more active than the original thorium salt (*18*). This observation led them to the discovery of a new member of the thorium series, which they called *thorium X*.

MME. CURIE AND HER DAUGHTER, MME. JOLIOT-CURIE

The latter has published many papers on the radioactive elements. During World War I, while still very young, she assisted her mother in the radiological service to the wounded. With her husband, Dr. F. Joliot of the Institut de Radium in Paris, she has prepared artificial radioactive elements.

R. B. Owens, Macdonald professor of electrical engineering at McGill University, and Sir Ernest Rutherford noticed that when a thorium compound is placed in an open vessel exposed to air currents, its radioactivity is not constant, and a study of this anomaly led them to the discovery that thorium gives off a gas, or emanation (*21*), (*31*), which is now known as *thoron*. It is an isotope of radon and actinon, and was the first radioactive gas to be discovered (*20*).

Professor Hans Geiger and E. Marsden noticed that the alpha particles from thoron are expelled at such very short intervals that they seem to be double. They found, as Rutherford suggested, that this strange behavior is caused by the presence of a very short-lived decay product of thoron, which they named *thorium A* (*80*). Prof. Geiger was born in Neustadt, Germany, and was educated at Erlangen, Munich. and Manchester. He is the director of the Laboratory for Radium Research at Charlottenburg.

Thorium A quickly decays into *thorium B*, another rather short-lived product, which spontaneously disintegrates, as shown by Rutherford, into *thorium C* (*53*). By heating a lead-encased platinum wire charged with the mixture to 700°, Miss J. M. W. Slater, Bathurst student at Newnham College, Cambridge, succeeded in volatilizing the thorium B* from the platinum and condensing it on the cold lead cylinder. At 1000° almost pure thorium C remained on the wire (*32*).

From "The Sphere"

THE CURIE FAMILY

It was shown by E. Marsden and Thomas Barratt and independently by Hahn and Meitner that thorium C* breaks down into *thorium C′* and *thorium C″* (*20*), (*34*), (*76*). The last member of this series, *thorium D*, or *thorio-lead*, ends what Soddy has called "the stately procession of element evolution" (*57*). Thus thorium "disintegrates in cascade" to form the successive products: mesothorium 1, mesothorium 2, radiothorium, thorium X, thoron, and thorium A, B, C, C′, C″, and D.

The explanation of the radioactive isotopes was given independently by Alexander S. Russell, Frederick Soddy, and Kasimir Fajans in 1913 (*90*). With the aid of Alexander Fleck at Glasgow, who had devoted three years to a thorough study of the chemical properties of the radioactive elements, Soddy deduced the following rule: The chemical properties of an alpha-ray product correspond with those of an element whose group number in the periodic system is *two less* than that of its parent.

A. S. Russell, Carnegie Research Fellow at the University of Glasgow, soon discovered the following corollary to this rule: The chemical prop-

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* Before 1911 the elements now known as *thorium B* and *thorium C* were called, respectively, *thorium A* and *thorium B*.

erties of a beta-ray product correspond with those of an element whose group number is *greater by one* than that of its parent.

That is, in an alpha-ray change, or expulsion of a helium atom with double positive charge, the atomic number (serial number of the element in the periodic system) decreases by two, and the atomic weight by four, units, whereas in a beta-ray transformation or emission of a negative electron, the atomic number increases by one unit while the atomic weight remains unchanged. Thus the combined effect of two beta-ray changes and one alpha-ray transformation is to produce an element which, like uranium 2,* is chemically identical with its great-grandparent. "Radioactive children," says Soddy, "frequently resemble their great-grand-

JEAN-FRÉDÉRIC JOLIOT*

Physicist and chemist at the Curie Institute. He has made many important researches on the phenomenon of recoil and the conservation of momentum, the electrochemical behavior of the radioelements, and on the expulsion of atomic nuclei and the existence of the neutron.

MME. JOLIOT-CURIE*

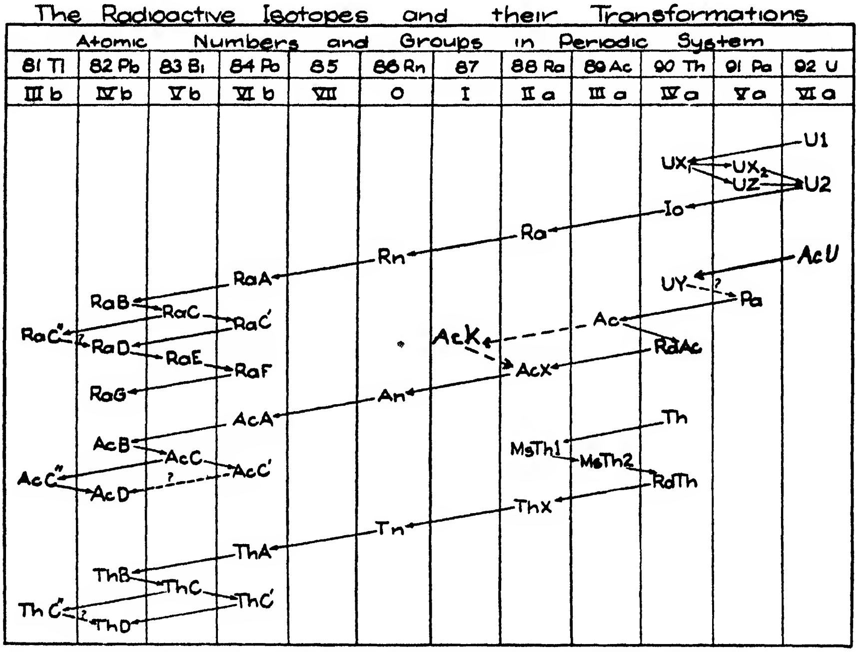
Daughter of Pierre and Marie Curie. She has made many original contributions to radioactivity and has collaborated with her husband and her mother in many brilliant researches. M. and Mme. Joliot and J. Chadwick have shown that when light elements like beryllium or boron are bombarded with swift α-particles, a highly penetrating stream of uncharged particles, or neutrons, is emitted. Each neutron is believed to consist of one positive proton and one negative electron closely bound together.

* Courtesy M. Freymann, Hermann et Cie., Paris.

parents with such complete fidelity that no known means of separating them by chemical analysis exists" (*56*).

The complete sequence of radioactive changes in the last twelve places in the periodic system which has been worked out through the researches of A. S. Russell, K. Fajans, F. Soddy, A. Fleck, and others, is given in the table reproduced herewith.

Thus it is evident that there are three natural radioactive isotopes of thallium, seven of lead, four of bismuth, seven elements in the polonium pleiad, three inert radioactive gases, four isotopes of radium, two of actinium, six of thorium, three eka-tantalums, and three uraniums.


The Radioactive Isotopes and their Transformations

LONG ARROWS POINTING TO THE LEFT REPRESENT α-RAY TRANSFORMATIONS; SHORT ONES POINTING TO THE RIGHT INDICATE β-RAY CHANGES

In 1903 M. and Mme. Curie, together with M. Becquerel, were awarded the Nobel Prize in chemistry. The Curie household with its two bright little daughters was a most happy one, and the gifted parents looked forward to a lifetime of united efforts for science. That dream was not to be fulfilled. On April 19, 1906, as Pierre Curie was crossing a busy street in Paris, he was struck by a heavy vehicle and instantly killed (*61*).

As a result of this frightful shock, Mme. Curie suffered a long, serious illness, but, when she finally recovered she resolved to devote the rest of her life to her children and to science. She taught the little girls herself, and for a time had charge of a small private school (*22*). The elder daughter, Irène (Mme. Joliot), has followed in the footsteps of her illustrious parents; while Ève, the younger one, has become a well-known concert pianist and has written a splendid biography which intimately reveals the great soul of Mme. Curie (*98*), (*105*).

Less than a year after her husband's death, Mme. Curie accepted a professorship at the University of Paris. With the able assistance of Professor André Debierne, who took charge of the laboratory and taught for many years an ever-increasing number of students from all parts of the world, she directed the instruction and research in radioactivity (*86*). When the university acquired new land, it laid out a street called the Rue Pierre Curie and built a laboratory for her. The Curie Institute and the Pasteur Institute work in close harmony, and Mme. Curie spent much of her time on researches dealing with the therapeutic properties of radium and radon (*69*). During World War I she had complete charge of the radiological service in French military hospitals.

In 1911 she was awarded the Nobel Prize in physics, and was thus the only person ever to have received the Nobel award twice. While radium with its dangerous yet beneficent radiations was prolonging countless lives, it was gradually undermining the health of its discoverer, and on July 4, 1934, her life of devotion to science and humanity came to a close (*97*).

Her years in the adopted country had given her a mode of expression that was truly French. She summarized her life story in these few words: "I was born in Warsaw of a family of teachers. I married Pierre Curie and had two children. I have done my work in France" (*1*).

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XXVII. RECENTLY DISCOVERED ELEMENTS

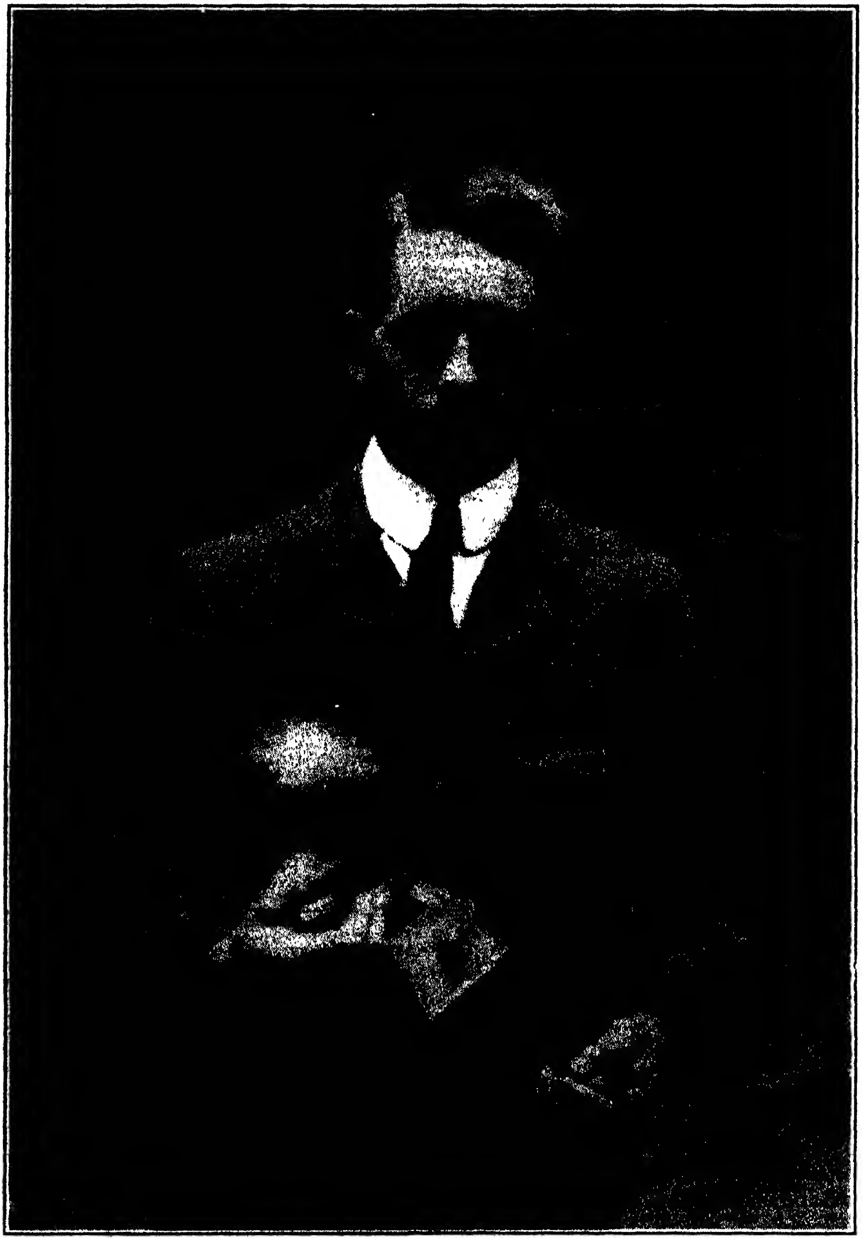
When H. G. J. Moseley discovered the simple relationship which exists between the X-ray spectrum of an element and its atomic number, there were seven unfilled spaces in the periodic table. Elements 43, 61, 72, 75, 85, 87, and 91 were yet to be revealed. Element 91 was discussed with the radioactive elements in Part XXVI. In 1923 D. Coster and G. von Hevesy showed that element 72, hafnium, is widely distributed but that it had escaped detection because of its close resemblance to zirconium. Elements 43 and 75 were announced by W. and I. Noddack in 1925, and the latter, rhenium, is now a commercial article. Element 61 was reported in 1926 by Hopkins, Harris, and Yntema and independently by other investigators in the United States and Italy. Elements 43 and 61 have been prepared in the cyclotron by bombarding molybdenum and neodymium, respectively, with deuterons; element 85, by bombarding bismuth with helions. Some of the radioactive substances which were artificially prepared by bombarding uranium with neutrons and which were at first thought to have atomic numbers higher than 92 have been shown to be fission products of the uranium nucleus. McMillan and Abelson found in 1940, however, that the 2.3-day activity is an isotope of element 93. H. Hulubei detected element 87 in pollucite with his curved-crystal X-ray focusing spectrograph. Mlle. Perey detected it as a short-lived isotope, actinium K, formed by α-ray disintegration of a small proportion of the atoms of actinium.

. . . . .

Beyond the violet seek him, for there in the dark he dwells,
Holding the crystal lattice to cast the shadow that tells
How the heart of the atom thickens, ready to burst into flower,
Loosing the bands of Orion with heavenly heat and power.
He numbers the charge on the center for each of the elements
That we named for gods and demons, colors and tastes and scents. . . . (1).

Although Mendeléeff's periodic system was a great aid in the search for new elements, there were some anomalies that it did not explain. The practical atomic weight of argon, for example, is higher than that of potassium, yet argon must precede potassium in the table, for there is no doubt whatever that it is an inert gas like helium and that potassium is an alkali metal like sodium. Tellurium and iodine present a similar discrepancy, and the radioactive isotopes were also the cause of much perplexity.

A much better basis of classification for the elements was finally found by a young English physicist in the course of his researches on X-rays. Henry Gwyn Jeffreys Moseley was born at Weymouth on November 23, 1887. While he was still a very young child he had the misfortune to lose his father, who was a distinguished zoölogist and professor at Oxford University. Moseley studied at Eton and at Trinity College, Oxford, and



Courtesy of the late Lyman C. Newell

HENRY GWYN JEFFREYS MOSELEY, 1887–1915

English physicist who studied the X-ray spectra of more than fifty elements and discovered the relation existing between the atomic number of an element and the frequency of the X-rays which it emits when bombarded by cathode rays. At the age of twenty-seven years he was killed while in active service at the Dardanelles.

received his master's degree in 1910. A year before his graduation he went to Manchester to discuss with Sir Ernest Rutherford the possibility of undertaking original research in physics (*30*).

After serving the University of Manchester for two years as lecturer and demonstrator in physics, he resigned his position in order to devote all his time to research, and was awarded the John Harling Fellowship. His colleagues soon recognized his superiority as an experimenter, and admired him because of his marvelous technique, broad knowledge of physics, cheerfulness, and friendly coöperation. When the British Association met in Australia in 1914, he entered enthusiastically into the discussion of atomic structure and gave an excellent report of his own researches on the X-ray spectra of the rare earths (*32*).

No scientist of the first rank ever had a shorter career. When Great Britain entered the war he immediately returned to England, entered the military service as a signaling officer, and on June 13, 1915, left for the Dardanelles. On the 10th of August, when he was telephoning an order to his division, a Turkish bullet passed through his head. His will, made while he was in active service, bequeathed all his apparatus and much of his private fortune to the Royal Society. Although Moseley was not quite twenty-eight years old at the time of his death, his researches had so revolutionized the study of atomic structure that his name will endure forever in the annals of science (*2*), (*36*), (*45*), (*46*).

Before entering the military service he had become intensely interested in Professor Laue's discovery that "the ordered arrangement of the atoms in a crystal would do the same for X-rays that a diffraction grating does for light" (*37*). When a target, or anticathode, is bombarded with cathode rays, it emits a beam of X-rays which is characteristic of the substance of which the target is made. With the help of Mr. C. G. Darwin, a grandson of the famous biologist, Moseley mapped the high-frequency spectrum of an X-ray tube provided with a platinum anticathode (*37*).

In the hope of finding some relationship between the frequency of the rays and the atomic number, or ordinal number of the element in the periodic table, he then carried out an elaborate investigation in which many different elements served as anticathodes. Upon examining these rays by diffracting them through a crystal, he found the following simple and beautiful relationship: When all the known elements are numbered in the order of their positions in the periodic system, the square root of the frequency of the X-rays emitted is directly proportional to the atomic number.

Thus Moseley's series is almost the same as Mendeléeff's series of increasing atomic weights. When, however, the elements are arranged, not according to their atomic weights, but according to their atomic numbers (Moseley numbers), the discrepancies between argon and potassium and between iodine and tellurium disappear (*31*).

Moseley's work not only shed much light on the periodic system and the relationships between known elements and the radioactive isotopes, but it was also a great stimulus in the search for the few elements remaining undiscovered (*47*). One of the first chemists to utilize the new method was Professor Georges Urbain of Paris, who took his rare earth preparations to Oxford for examination. Moseley showed him the characteristic lines of erbium, thulium, ytterbium, and lutecium, and confirmed in a few days the conclusions which Professor Urbain had made after twenty years of patient research. The latter was greatly surprised to find that a scientific contribution of such fundamental importance had been made by one so young, and immediately began to teach Moseley's method of X-ray analysis. "His law," said he, "substituted for the rather romantic classification of Mendeléeff a precision entirely scientific" (*36*).

A. V. Grosse (*93*) has recently shown, however, that, when one substitutes for the practical atomic weight of each element the *arithmetic mean* of the atomic weights of all its isotopes, "the row of increasing atomic weights is identical with the sequence of increasing nuclear charges" and the discrepancies formerly presented by argon and potassium, cobalt and nickel, tellurium and iodine, and thorium and protoactinium no longer exist.

Hafnium (Element 72)

Moseley stated that, within the limits of his researches, which covered all the elements between aluminum (number 13) and gold (number 79), there were spaces for three missing ones: numbers 43, 61, and 75, and that, since their X-ray spectra can be accurately predicted, it ought to be rather easy to find them. It was then believed that the *celtium* whose arc spectrum Professor Urbain had described in 1911 was element 72 (*3*), (*36*), (*56*).

However, when Moseley and Urbain examined the rare-earth residues supposed to contain the new element, they found only about ten lines, all of which could be attributed to lutecium and ytterbium. In 1922, after a long period of interruption because of military duties, Professor Urbain resumed his search for element 72 in the same rare-earth residues which he and Moseley had examined before the war. At his suggestion M. A. Dauvillier used de Broglie's improved method of X-ray analysis and observed two faint lines which almost coincided with those predicted for element 72 (*33*), (*54*).

After titanium was discovered in 1791 by the Reverend William Gregor in Cornwall, its atomic weight was determined by such able chemists as H. Rose, Mosander, and Dumas, but the results showed such great discrepancies that Mendeléeff predicted that another element would be found in titanium ores (*4*). It was in zirconium ores, however, that large quantities of element 72 were finally revealed (*34*), (*38*), (*42*).

On the basis of his quantum theory of atomic structure, Niels Bohr believed that, since Urbain's *celtium* had been obtained from the rare earths, it could not be element 72, for the latter must be quadrivalent rather than trivalent and must belong to the zirconium family. He showed that the chemical properties of an atom are determined by the number and arrangement of the electrons within it and especially by the number and arrangement of the outermost ones, the so-called "valence electrons." Since there is usually an appreciable difference in the outer electrons of two adjacent elements in the periodic system, there is also, as a rule, a marked difference in chemical properties. In the rare-earth group, however, and in the triads of the iron and platinum families, the only structural differences are in the deeper shells of the atoms, and therefore these elements are more difficult to separate. According to Bohr's theory these deep-seated differences in the rare earths lie in the interval between lanthanum (element 57) and lutecium (element 71). Element 72 should, however, according to his theory, be quite different from lutecium in the constitution of its outer group of electrons, and should therefore exhibit properties entirely different from those of the rare earth elements (*54*), but closely resembling those of zirconium. Bohr therefore advised Dr. Hevesy to search for this element in zirconium ores (*5*), (*28*).

Courtesy Cornell University

GEORG VON HEVESY

Professor at the Institute of Theoretical Physics, Copenhagen. Hungarian chemist who, with Dr. Dirk Coster of the University of Groningen, discovered the element hafnium in zirconium ores and made a thorough study of its properties. Author of many papers on chemical analysis by X-rays, radioactivity, the rare earths, and electrolytic conduction.

It was in January, 1923, that Dirk Coster and Georg von Hevesy in Copenhagen brought their search for the new member of the zirconium family to a successful conclusion. Its discovery in zirconium ores was made possible by Moseley's method of X-ray analysis, and it was Coster's previous work in the same field that enabled him to recognize the new element (*2*).

Although they named it *hafnium** for the city of Copenhagen, neither of these investigators is Danish. Professor Coster lives in the Netherlands

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*** Both sides of the controversy regarding the name of element 72 are presented in the English journals, *Nature* and *Chemistry and Industry* (*28*), (*54*).**

and Professor von Hevesy is a Hungarian. The former is a professor of physics and meteorology at the Royal University of Groningen and director of the physical laboratory. The Dutch, French, English, German, and American journals contain many of his papers on such subjects as X-ray spectra, theory of atomic structure, Stokes's law in the L-series of X-rays, and the rotational oscillation of a cylinder in a viscous liquid.

Professor von Hevesy was born in Budapest in 1885 and was educated in the universities of Budapest, Berlin, and Freiburg. His researches have brought him into close contact with such famous scientists as Haber at Karlsruhe, Rutherford at Manchester, and Donnan at Liverpool, and the X-ray investigation with Dr. Coster which resulted in the discovery of hafnium was carried out while both were connected with Bohr's Institute of Theoretical Physics at Copenhagen. Professor von Hevesy taught for a time as professor of physical chemistry at the University of Freiburg. In 1930 he served as the George Fisher Baker Non-Resident Lecturer in Chemistry at Cornell University. His researches have been in the fields of physical chemistry, electrochemistry, radioactivity, and the separation of isotopes (*6*).

DIRK COSTER

Professor of physics and meteorology at the Royal University of Groningen. Co-discoverer with Georg von Hevesy of the element hafnium. Author of many papers on X-rays and atomic structure.

Hafnium had lain hidden for untold centuries, not because of its rarity but because of its close similarity to zirconium (*54*), and when Professor von Hevesy examined some historic museum specimens of zirconium compounds which had been prepared by Julius Thomsen, Rammelsberg, Nordenskjöld, Marignac, and other experts on the chemistry of zirconium, he found that they contained from 1 to 5 per cent of the new element (*26*), (*55*). The latter is far more abundant than silver or gold. Since the earlier chemists were unable to prepare zirconium compounds free from hafnium, the discovery of the new element necessitated a revision of the atomic weight of zirconium (*7*), (*28*).

Professor von Hevesy and Thal Jantzen separated hafnia from zirconia by repeated recrystallization of the double ammonium or potassium fluorides (*26*), (*38*). Metallic hafnium has been isolated and found to have the same crystalline structure as zirconium. A small specimen of the first metallic hafnium ever made is on permanent display at the American Museum of Natural History in New York City. Dr. von Hevesy, who prepared it, presented it to the Museum for the collection of chemical elements (*138*). A. E. van Arkel and J. H. de Boer prepared hafnium by passing the vapor of the tetraiodide over a heated tungsten filament (*26*), (*53*).

Eka-manganese and Rhenium (Elements 43 and 75)

Two new elements of the manganese group, numbers 43 (eka-manganese) and 75 (dwimanganese), were announced in June, 1925, by the German chemists, Dr. Walter Noddack and Dr. Ida Tacke of the Physico-Technical Testing Office in Berlin and Dr. Otto Berg of the Werner-Siemens Laboratory. The discovery was not accidental, but the result of a long search in platinum ores and in the mineral columbite (*15*). Platinum ores contain the elements 24 to 29, 44 to 47, and 76 to 79 (chromium to copper, ruthenium to silver, and osmium to gold), whereas columbite contains numbers 39 to 42 and 72 to 74 (yttrium to molybdenum, and hafnium to tungsten). Hence it was hoped that one or both of these sources might yield the missing elements, 43 and 75.

Upon studying the relative frequencies of known elements in the earth's crust, Noddack, Tacke, and Berg found that those of odd atomic number are less common than those of even number, and from the known frequency of occurrence of platinum ores and of columbite they obtained an approximate idea of the extent to which they would have to carry their processes of extraction. Moreover, since elements 43 and 75 belong to the manganese group, many of their physical and chemical properties could be predicted. Element 75 was finally separated from columbite, and named *rhenium* in honor of the German Rhine (*8*), (*39*). The difficult concentration processes were carried out by Drs. Noddack and Tacke alone, but Dr. Berg assisted in making the observations with the X-ray spectroscope (*40*). They also observed some X-ray lines which they attributed to element 43, which they named *masurium* for

J. HEYROVSKÝ

Professor of physical chemistry at Charles University, Prague. Author of an "Introduction to Radioactivity." With E. Votoček he edits the *Collection of Czechoslovak Chemical Communications*, a monthly journal published in French and English to make the contributions of Czechoslovakian and Russian chemists accessible to those who do not read the Slavonic languages.

Masurenland, East Prussia. Before the discovery of rhenium, manganese had no companions in sub-group *VIIa* of the periodic system.

On September 5, 1925, Fräulein Tacke lectured on the new elements before the Verein deutscher Chemiker in Nuremberg (*9*). After thanking her for the address, the president mentioned that this was an historic occasion, for it was the first time that a woman had ever spoken before the Verein. He also expressed the hope that other "*Chemikerinnen*" might soon follow her example. Fräulein Tacke and Dr. Noddack have since been united in marriage and have continued their joint researches. Largely through their efforts, the knowledge of rhenium has rapidly increased, and the chemical, physical, and analytical properties of a large number of its compounds have been accurately determined. In recognition of their discoveries they have been awarded the Liebig Medal.

Courtesy Scientific Monthly

WILLIAM FREDERICK MEGGERS

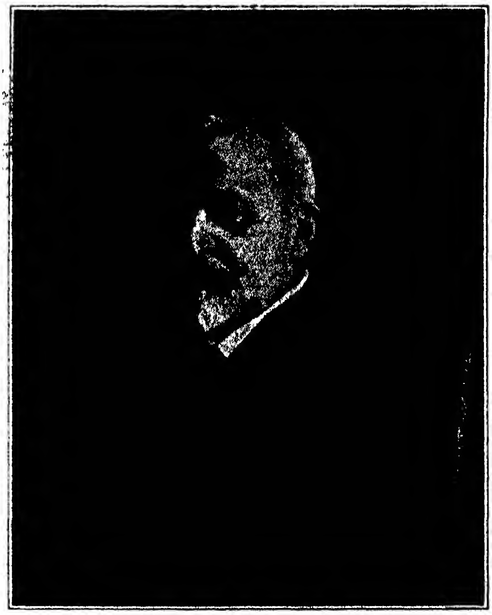
Physicist at the U. S. Bureau of Standards since 1914. Chief of the spectroscopy section. Author of many papers on optics, astrophysics, photography, measurement of wave-length standards, and description and analysis of spectra. The instrument in the foreground is a concave grating spectrograph, used for photographing the emission spectrum of rhenium (*43*).

In 1925 F. H. Loring and J. G. F. Druce in England and V. Dolejšek and J. Heyrovský in Czechoslovakia independently announced that commercial manganese salts and even so-called "pure" preparations contain small amounts of element 75 (*57*), (*58*), (*59*). While searching for an element of atomic number 93, the English chemists removed manganese and other heavy metals by precipitation as the sulfides, and evaporated the filtrate to dryness. X-ray analysis of the residue apparently revealed lines of element 75.

Dr. J. Heyrovský, professor of physical chemistry at the Charles University of Prague, and Dr. Dolejšek of the Prague Academy of Sciences thought they detected element 75 in manganese salts by a different method. They examined some manganese solutions with their dropping mercury cathode, plotted the current intensity as ordinates against the applied electromotive force as abscissas, and noticed a peculiar "hump" in the curve in the region between −1.00 and −1.19 volts from the potential of the calomel electrode. After showing that zinc, nickel, cobalt, and iron were absent, Heyrovský and Dolejšek suspected the presence of the undiscovered eka-manganeses, elements 43 and 75. Using their dropping mercury cathode in conjunction with a polarograph, they obtained automatically a permanent record of the electrolytic reaction.

After dipping strips of zinc into concentrated solutions of manganese salts, they scraped off a deposit containing zinc, lead, cadmium, nickel, and cobalt. After complete removal of these heavy metals by precipitation as the sulfides, they found no evidence of element 43, but thought they found the X-ray lines of number 75 (*44*). When Dr. Druce took his dwimanganese preparation to the Charles University in Prague for polarographic examination, the Czechoslovakian chemists confirmed his conclusions.

In response to criticism by the Noddacks and by L. C. Hurd (*69*), who was unable to detect rhenium in any of the various manganese salts which he studied, Dr. Heyrovský himself afterward worked out a sensitive polarographic test for the *absence* of rhenium in manganese salts. Although potassium perrhenate gives a polarographic step at −1.2 volts from the normal calomel zero, this is not conclusive evidence for rhenium in presence of cobalt, iron, nickel, or zinc. When, however, he added sodium acetate, acetic acid, and hydrogen sulfide to precipitate these metals, the perrhenate was changed to Re_2S_7 or thioperrhenate, without precipitating, and the "step" was shifted. In the absence of perrhenate, this shift does not occur. Upon testing various commercial manganese salts in this manner, Professor Heyrovský found that they contain less than one part of rhenium per million parts of manganese and that the polarographic steps



J. Heyrovský, Czechoslov. Chem. Communications

BOHUSLAV BRAUNER, 1855–1935

Professor of chemistry at the Bohemian University of Prague. He made brilliant contributions to analytical chemistry, the determination of atomic weights, and the chemistry of the rare earths. In 1902 he predicted the existence of element 61, now known as illinium.

Courtesy University of New Hampshire

Charles James, 1880–1928

Director of the chemistry department at the University of New Hampshire. Author of many papers on the rare earths. Independent discoverer of lutecium and illinium. He was born in England and studied under Sir William Ramsay.

at −1.0 and −1.2 volts shown on polarograms of manganese solutions, as well as the lines of the X-ray spectrum, must be due to elements other than rhenium (*77*). Although the polarograms were at first misinterpreted in this case, the polarographic method has nevertheless been used successfully in various other analyses (*89*).

B. SMITH HOPKINS, PROFESSOR OF CHEMISTRY AT THE UNIVERSITY OF ILLINOIS

Discoverer of illinium (element 61). His researches on the rare earths and atomic weights and his investigation of the magneto-optic method of chemical analysis are well known.

In 1937 C. Perrier, E. Segrè, and B. N. Cacciapuoti at the Royal University at Palermo reported the presence of radioactive isotopes of element 43 in a molybdenum target which had been bombarded with deuterons for many months in the Berkeley cyclotron (*96*), (*114*). They studied some of its chemical properties, observed the K_α line of its X-ray spectrum (*117*) and stated that "this is the first time that the X-ray line of a new element, synthesized artificially, has been observed." The K-lines of this element are emitted spontaneously as a consequence of the transition from an upper to a lower excitation state of the nucleus (*139*). Since no stable isotope of element 43 was available, Perrier and Segrè carried out the chemical identification with the aid of rhenium as a carrier (*122*). They found that, in its chemical properties, element 43 resembles rhenium more closely than it resembles manganese (*135*). Like rhenium, it is precipitated by hydrogen sulfide from alkaline or moderately concentrated acid solution (*122*). Element 43 can also be produced by bombarding molybdenum with neutrons or by bombarding columbium with alpha-particles (*139*), (*145*). According to the well-founded rules of Josef Mattauch, no stable isotopes of element 43 are to be expected. This may explain why it has never been prepared and concentrated from natural products (*139*).

Although element 43 has never been concentrated and purified, Colin G. Fink and P. Deren of Columbia University in 1934 perfected a process for electroplating rhenium as a bright, hard deposit which is surprisingly resistant to hydrochloric acid (*76*). Dr. William F. Meggers of the United

States Bureau of Standards has made a thorough study of the arc spectrum of rhenium (*43*).

Illinium (Element 61)

All the rare-earth elements except one were found before the introduction of X-ray spectroscopy. In the estimation of Professor von Hevesy,

> . . . to have discovered and isolated nearly all of the rare earths without further guidance, in spite of their great similarity and the great rarity of some of these, is one of the most brilliant accomplishments that experimental chemistry has ever produced (*38*).

LABORATORY FOR RARE-EARTH FRACTIONATION AT THE UNIVERSITY OF ILLINOIS*

The four large earthenware utensils in the left foreground are stone filters. On the desk in front of these are four 90-liter evaporating dishes with stirring devices and reagent bottles in position. These evaporating dishes are mounted on wash-tubs which serve as steam baths. The reagents are added from the large bottles by compressed air. These are used in the early stages of the rare-earth work when the volume of material used is large. On the desk toward the right are flasks containing rare-earth fractions just as they are used in the process of fractional crystallization.

As early as 1902, the late Professor Bohuslav Brauner of the Bohemian University of Prague, a friend of Mendeléeff, predicted the existence of an element between neodymium and samarium (*11*). It was noticed that there is a sudden change in certain properties of the rare-earth ele-

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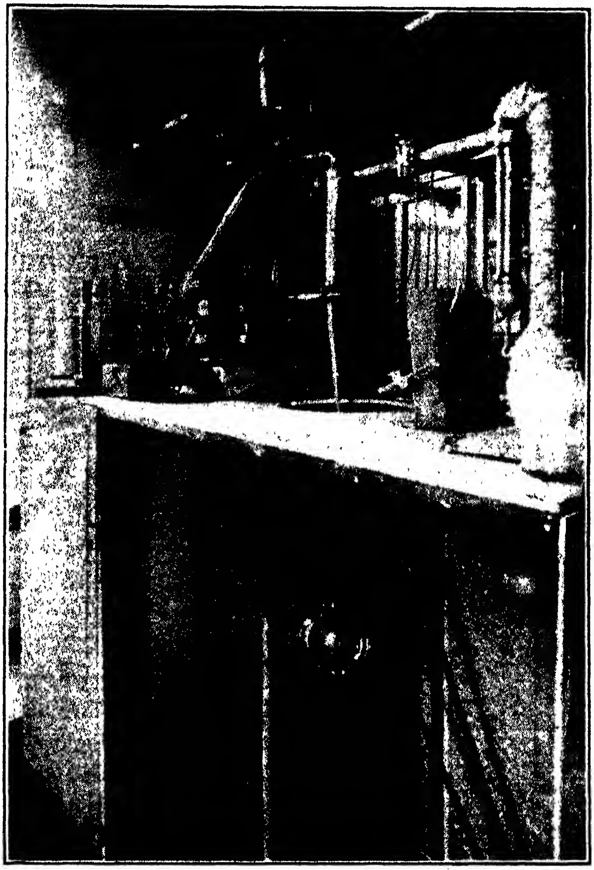
* The above photograph and description were graciously contributed by Dr. B. Smith Hopkins.

ments at this point: the double magnesium rare-earth nitrates differ, for example, by nearly equal increments except in the case of neodymium and samarium, whereas these two elements can be sharply separated by fractional crystallization.

This method of fractionation of the double magnesium nitrates was introduced by the late Professor Charles James of the University of New Hampshire (*41*), who worked for years in an attempt to reveal the missing rare-earth element, the existence of which seemed all the more probable after Moseley had disclosed the vacant place for element 61. In 1926, while Professor J. M. Cork was using the excellent X-ray apparatus at the University of Michigan to examine some rare-earth material that had been carefully purified by Professor James and H. C. Fogg in New Hampshire, Professor B. Smith Hopkins and his colleagues at the University of Illinois announced the discovery of the elusive element (*18*), (*22*), (*41*)



X-RAY APPARATUS AT THE UNIVERSITY OF ILLINOIS*

In the lower center is the kenetron. On a shelf above it is the vacuum chamber for the X-ray apparatus. The metal X-ray tube itself projects from the front of the vacuum chamber toward the observer's right. At the right of the picture is the liquid-air trap which serves to keep mercury out of the vacuum chamber.

Since monazite sand contains neodymium (element 60) and samarium (element 62), Professor Hopkins thought that it might reasonably be

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* The above photograph and description were graciously contributed by Dr. B. Smith Hopkins.

expected to contain element 61 also. The Lindsay Light Company and the Welsbach Mantle Company presented him with some rare-earth residues from monazite, from which the thorium and part of the cerium had been removed for the manufacture of Welsbach gas mantles, and from which he prepared some very pure neodymium and samarium salts to send to the United States Bureau of Standards. Spectroscopic examination revealed a number of new lines which were common to both samples (*18*), (*20*).

Professor Hopkins and Dr. Harris recrystallized the bromates rather than the double magnesium nitrates. Since the double magnesium nitrates have solubilities which increase with atomic number, fractionation by this method separates the elements in the order of their atomic numbers and brings element 61 between neodymium and samarium, which are relatively abundant. When the bromates are recrystallized, however, neodymium goes into the more soluble fractions, and the order of crystallization is: europium (which has the least soluble bromate), samarium, gadolinium, element 61, terbium, and neodymium (*21*), (*23*). Although neodymium and samarium obscure the presence of other elements, terbium and gadolinium do not have this troublesome property.

LUIGI ROLLA, PROFESSOR IN THE FACULTY OF SCIENCES AT THE ROYAL UNIVERSITY OF FLORENCE

Director of the Institute of Inorganic Chemistry. Author of papers on the rare earths in the atmospheres of the stars and on ionization potentials with relation to the periodic system of the elements.

Professor Hopkins was assisted in these researches by Dr. J. Allen Harris and Dr. Yntema. The fractionations were made at Urbana, while Dr. Yntema, a Fellow of the National Research Council, made the X-ray examination in the Sloane Laboratory of Physics at Yale (*25*). After five years of searching, an inspiring thing happened. Just as in Tschaikowsky's "1812 Overture" the strains of the French hymn fade away in the triumphant swelling of the Russian anthem, so in Professor Hopkins' spectra the neodymium lines faded out and the new lines (5816 A. U. and 5123 A. U.) of the absorption spectrum became stronger; moreover, the lines of the X-ray spectrum were found to coincide with those predicted from Moseley's rule. Thus element number 61, illinium, the last of the rare earths, took its place in the periodic table (*10*), (*18*), (*21*), (*24*), (*95*).

B. Smith Hopkins was born at Owosso, Michigan on September 1, 1873, and was educated at Albion College, Columbia University, and The Johns Hopkins University. He has taught at Nebraska Wesleyan University, at Carroll College in Wisconsin, and, since 1912, at the University of Illinois, and thousands of students remember his kindly encouragement, his unassumed modesty, and his generous fairness in judging the contributions of other investigators of the rare earths. He has published a number of books, including two on the rarer elements (*12*), and is the first American to fill one of the vacant places in the periodic table. Professor Boltwood's ionium, although it has specific radioactive properties, is chemically inseparable from thorium.

Since the rare-earth preparations of Professor James exhibited the lines of illinium when examined with the X-ray spectroscope, he is to be regarded as an independent discoverer of the element. His early attempts to reveal this missing element and his other contributions to the chemistry of the rare earths have been ably discussed by B. Smith Hopkins (*41*) and by H. A. Iddles (*52*).

Professor Luigi Rolla of the Royal University of Florence thought for a time that he had discovered element 61, which he called *florentium* (*13*), (*14*), (*19*). His method consisted in separating some didymium material from Brazilian monazite and fractionating it as the double thallium sulfates. When Miss Rita Brunetti of Arcetri, a professor at the Institute of Inorganic and Physical Chemistry at the University of Florence, examined the X-ray absorption spectra of the K series, she concluded that a new element must be present. Professor Rolla's results were deposited as a sealed package with the *Reale Accademia dei Lincei* in June, 1924. The contents were not published, however, until November, 1926 (*19*), (*29*). These Italian scientists have done excellent work on the rare earths.

Some chemists, including Drs. Prandtl and W. and I. Noddack, have been unable to confirm the existence of element 61 (*72*), (*73*). Dr. Hopkins and his collaborators, however, are continuing their remarkable researches on the rare earths in the hope of concentrating this elusive element. Although Maurice Curie and S. Takvorian (*70*) in 1933 observed an apparently new penetrating radiation from a neodymium-samarium fraction in which they had attempted to concentrate element 61, they later found that this radiation was due, not to element 61, as they had supposed, but to actinium and its disintegration products. They had previously published several reports of unsuccessful attempts to verify the existence of this element and, for a time, believed that they had finally detected it (*74*), (*75*).

In 1933 L. Rolla and L. Mazza studied the radioactivity of neodymium, of samarium, and of mixtures of these two rare earths, which they had prepared from a ton of commercial didymium. They concluded that "the existence of a radioactive element 61 is, in our opinion, very uncertain, and the slight variations of activity verified in the different samples of samarium and the very weak activity of neodymium, at least, are not to be attributed to this element" (*143*). Since, on the basis of Mattauch's rules, stable isotopes of element 61 are not to be expected, it is not surprising that it has never been possible to prepare this element from natural sources, concentrate it, and study its properties (*139*).

In 1938 M. L. Pool and L. L. Quill bombarded neodymium with deuterons from the cyclotron at the University of Michigan and obtained a radioactive product with a half-life period of 12.5 hours, which they believe may belong to element 61 (*124*), (*125*), (*126*). When Emilio Segrè and Chien Shiung-Wu bombarded some rare earths sent them by L. Rolla, they obtained a short-lived radioactive product which may have been element 61 (*134*). Several types of bombardments, as, for example, that of praseodymium with alpha-particles, may possibly yield radioactive isotopes of element 61 (*139*). Its properties, however, must resemble those of the other rare earth metals so closely that chemical identification of minute traces of it would be exceedingly difficult.

Eka-cesium (Element 87)

Speculations have long been made as to the probable nature of element 87, the unknown alkali metal, and element 85, the unknown halogen, and many carefully planned searches for them have failed. Since both of these unfilled spaces lay in the radioactive region of the periodic system, and since no inactive isotopes of elements having atomic numbers greater than 83 had ever been found, Professor von Hevesy thought that elements 85 and 87 ought to be radioactive, and that they might possibly be formed by disintegration of radon, mesothorium 2, or polonium, or their isotopes (elements 86, 89, or 84). From the rule deduced by Soddy, Fajans, Fleck, and Russell, he reasoned that element 87 might be an alpha-ray product of element 89 or a beta-ray product of element 86 and that element 85 might be formed by alpha-disintegration of the unknown element 87 or by beta-disintegration of a polonium isotope (*60*).

C. F. Graham believes, however, that, "since the radioactive degeneration series does not pass through the element [87], there is no reason to expect that it will be radioactive to any greater degree than the other alkali elements" (*61*).

While Druce and Loring were searching for element 93, they observed a faint but clear X-ray line between the theoretical $L\alpha_1$ and $L\alpha_2$ lines of element 87 (*63*).

Between 1929 and 1932 Dr. Fred Allison and his collaborators published several papers on his magneto-optic method of analysis, by means of which he reported evidence of the presence of element 87 (which he called *virginium*) in lithium and cesium minerals (*17*), (*48*), (*49*), (*50*), (*51*), (*62*), (*64*), (*66*), (*68*), (*71*), (*78*). The validity of this method of analysis, however, has not been satisfactorily verified.

In October, 1931, Professor Jacob Papish and Eugene Wainer of the chemistry department at Cornell University obtained spectroscopic evidence of the existence of this element. In searching for it they believed that it must bear some resemblance to cesium and radium, that its primary spectral lines must lie in the infra-red (*27*), (*35*), and therefore be difficult to observe when the eka-cesium is present in low concentrations, and that, since the electroscope had not already revealed it, it could not be appreciably radioactive. These assumptions led them to search for the missing element in a specimen of samarskite which was rich in uranium and its disintegration products and which also contained rubidium and cesium. By repeated recrystallization of the aluminum alums prepared from this material, they obtained a fraction which exhibited five of the X-ray spectrographic lines predicted from Moseley's rule. These lines were produced, as might be expected, by the fractions containing the least soluble alums (*27*). The Cornell chemists were unable to verify the magneto-optic observations of Professor Allison and his colleagues. The Noddacks, in spite of careful search in minerals reputed to contain them, have been unable to detect either element 61 or 87 (*72*). Professor Gustave A. Aartovaara of the Helsingfors Technical University reported the presence of element 87 in Finnish feldspars (*65*), (*67*).

Early in 1937 Dr. F. R. Hirsh, Jr., at Cornell University prepared some cesium hydrogen sulfate from lepidolite and studied its X-ray spectrum, using the same calcite crystal which Papish and Wainer had used (*101*). Since the faint narrow band which Dr. Hirsh at first took to be the $L\alpha_1$ doublet of eka-cesium was broader than an L X-ray line such as thorium $L\alpha_{1,2}$, he replaced the cesium acid sulfate target by a blank copper wedge. The faint narrow band still appeared in the place where the $L\alpha$ doublet of element 87 ought to be. Dr. Hirsh therefore believes that this line was probably caused by a flaw in the calcite crystal. When he eliminated the effect of this flaw by oscillating the crystal, the supposed line of element 87 disappeared.

Professor Horia Hulubei in Paris, however, extracted the alkali metals from pollucite and believes that he has detected in them the $L\beta_1$ and $L\beta_2$ lines of eka-cesium with his curved crystal focusing spectrograph. He has proposed for element 87 the name *moldavium* and the symbol *Ml* "in honor of the Roumanian province Moldavia on the eastern frontier of Latin Culture" (*102*), (*129*). This X-ray spectrograph was perfected by Dr. Jesse W. M. Du Mond and Dr. Harry Kirkpatrick at the California Institute of Technology (*103*) and Mlle. Yvette Cauchois at the Laboratory of Physical Chemistry in Paris (*104*). Mlle. Cauchois has collaborated for several years with Professor Hulubei, who was formerly in charge of the physical laboratory at the University of Jassy, Roumania.

Stefan Meyer, V. F. Hess, and F. A. Paneth of Vienna observed in 1914 that pure actinium undergoes a dual disintegration. Although most of its atoms emit beta-particles, a few atoms (fewer than 1 per cent of them) give off alpha-particles, thus forming element 87 (actinium K) (*136*), (*137*). Although these researches were interrupted by the First World War, Mlle. Marguerite Perey of Paris confirmed them in 1939. (See the table of radioactive isotopes and their transformations on page 506.)

From a study of actinium which had been freed from all its products of disintegration, Mlle. Perey believes that the β-activity with the period of 21 minutes which she observed is due to the formation of element 87 by α-ray disintegration of actinium. Since this β-activity is not carried down with ceric hydroxide, lead sulfide, or barium carbonate, and since it is co-precipitated with cesium perchlorate, it must belong to an alkali metal. She has observed an α-activity with a range of 3.5 centimeters in air from the purified actinium and has shown that it cannot be attributed to protoactinium. She believes that her 21-minute β-activity is caused by a short-lived isotope of Professor Hulubei's moldavium (*118*) (*130*).

Eka-iodine (Element 85)

The validity of the magneto-optic method of analysis, on the basis of which Dr. Fred Allison and his collaborators reported the presence in monazite sand of element 85 (which they called alabamine), has never been adequately confirmed by chemists in other laboratories (*16*), (*50*), (*62*), (*79*), (*81*).

The preparation of element 43 in the 37-inch Berkeley cyclotron in 1937 suggested the possibility of preparing element 85 (eka-iodine) in a similar manner. Since alpha-particles possessing energy in excess of 20,000,000 electron volts would be needed to transmute bismuth into eka-iodine, this attempt had to be postponed until the completion of the 60-inch Berkeley cyclotron, which was designed and constructed by Ernest O. Lawrence and his colleagues (*124*). In 1940 D. R. Corson, K. R. MacKenzie, and Emilio Segrè bombarded a water-cooled bismuth target with alpha-particles, or helions, having an energy of 32,000,000 electron volts (*122*), (*123*), (*124*), (*139*).

Although element 85 had long been known as "the unknown halogen," they found that it bears more resemblance to polonium and bismuth than to iodine and that it has marked metallic properties. After filing off the surface of a bombarded bismuth target and dissolving the filings in concentrated nitric acid, they investigated the chemical properties of the artificially produced radioactive product. Although they were dealing with only minute, unweighable quantities of this element, its radioactivity made possible a study of many of its chemical properties as it was precipitated with various carriers. It is precipitated with hydrogen sulfide in acid solution, is not precipitated by silver ion, and can be electroplated on several metals. When plated on bismuth, it can be sublimed off and collected as a pure, invisible, radioactive layer (*139*). According to J. G. Hamilton and M. H. Soley, eka-iodine has a half-life of 7.5 hours, but differs from all other artificially produced radio-elements in that it emits alpha-particles (*124*).

Walter Minder, a Swiss physicist at the Radium Institute in Berne, has given evidence of the production of an isotope of element 85 by beta-disintegration of radium A and has proposed for it the name *helvetium* (*Hv*) (*123*), (*127*). H. Hulubei and Mlle. Yvette Cauchois have also produced evidence for the existence of this element in the decay products of radon (*123*), (*128*). Dr. Minder and Alice Leigh-Smith, who studied under Mme. Curie and later carried on research at the Röntgen Institute in Berne, believe that they have also found experimental evidence of the existence of element 85 in the thorium family (*140*). Drs. J. G. Hamilton and M. H. Soley have shown that it is concentrated in the thyroid glands of guinea pigs and rapidly excreted as iodine is (*123*), (*124*). They suggest that it may, therefore, have potential value in the treatment of hyperthyroidism in human beings (*124*).

A large amount of careful research must still be done before the chemical and physical properties of elements 43, 61, 85, and 87 are made manifest.

Artificial Radioactivity*

The creation, by neutron bombardment of uranium, of the so-called "transuraniums" is based on the discovery of artificial radioactivity by M. and Mme. Joliot-Curie. Irène Curie was born in Paris in September, 1897, the elder daughter of M. and Mme. Pierre Curie of honored memory. Both in Poland and in France she had many relatives who were devoting their lives to science, and from her earliest childhood she has lived in a scientific atmosphere, among distinguished chemists and physicists. When Irène was less than a year old, her mother discovered the radioactive element polonium, which was destined to play an important part in the later researches of both mother and daughter. A few months later M. and Mme. Curie discovered another element of even greater importance, which they named radium.

While they were patiently carrying out the laborious but brilliantly exe-

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* The section on artificial radioactivity was first published in April, 1936, for the Kansas City Meeting of the American Chemical Society.

cuted investigations on which the science of radioactivity is based, Irène was left under the affectionate care of her grandfather, Dr. Eugène Curie, a cultured physician, well versed in the sciences. When she was seven years old, her parents, together with Henri Becquerel, were awarded the Nobel Prize in physics. Mme. Curie once said, "As our elder daughter grew up, she began to be a little companion to her father, who took a lively interest in her education and gladly went for walks with her in his free times, especially on his vacation days. He carried on serious conversations with her, replying to all her questions and delighting in the progressive development of her young mind" (*105*). When Irène Curie was only eight years old, however, she suffered the cruel loss of her affectionate father, who was killed in a traffic accident.

She received her earliest instruction from two Polish governesses, one of them a cousin of Mme. Curie. Thus she soon learned to understand and love the language and culture of her mother's native country. After studying for a time in a private school in Paris, she attended for two years a coöperative school in which Mme. Curie and other members of the university staff united to give their own children the advantages of a well-balanced literary, artistic, scientific, and physical education in which practical experiments played a large part. According to Mme. Curie, Irène "resembled her father in the form of her intelligence. She was not quick, but one could already see that she had a gift of reasoning power and that she would like science." As a girl of fourteen, Irène went to Stockholm to witness the solemn, inspiring ceremony in which her mother was awarded the Nobel Prize in chemistry. Mlle. Curie later attended a Paris college, passed her bachelor's examination at an unusually early age, and continued her scientific studies at the Sorbonne.

During and after the World War, Mme. Curie established many radiological stations and radiologic motor cars, with which she taught volunteer helpers how to use Röntgen-ray equipment in the examination of the wounded. This made it possible to determine the exact location of projectiles and to save many men from death or permanent disability. On several of her trips to the ambulance stations in the war zone, Mme. Curie was accompanied by Irène, who was then only seventeen years old. Although she was just beginning her advanced studies at the Sorbonne, Mlle. Curie, eager to be of service, studied nursing and radiology, and did ambulance work at the front, for which, at the close of the war, she was awarded a medal. In 1916 a department of radiology was added to the Nurses' School, where, according to Mme. Curie, "a few persons of good will, among them my daughter" trained one hundred and fifty operators. Throughout the entire duration of the war, Mme. Curie took almost no vacation. "My older daughter," said she, "would scarcely take any, and I was obliged to send her away sometimes to preserve her health. She was continuing her studies in the Sorbonne, and . . . was helping me with my war work."

In 1921 Mme. Curie visited the United States, where she received many honors, including the gift of a gram of radium from the women of America. Irène and her younger sister, Ève-Denise, accompanied their mother on this visit.

In the same year Mlle. Curie published in the *Comptes rendus* her first scientific paper, which was entitled "The atomic weight of the chlorine in certain minerals." Upon examining three chlorine minerals (a Canadian sodalite, a Norwegian chlor-apatite, and a sample of sodium chloride from a Central African desert, which had probably been formed by the weathering of local Archaean granites), she found the chlorine in the first two to be identical within the experimental error of 0.02 atomic weight unit with that in an ordinary chloride. "The results concerning the sodalite and the apatite lead one to think," said she, "that in general the atomic weight of the chlorine contained in ancient minerals scarcely differs from that of normal chlorine from sea water; if this result were generalized, one would be led to conclude that there was a very perfect mingling of the two isotopes before the formation of the mineral or rather that the two isotopes were formed from the beginning in a practically constant proportion." The chlorine in the sodium chloride from the African desert apparently had a higher atomic weight, however, for Mlle. Curie obtained 35.60 for its atomic weight, even though bromine and iodine were absent (*106*).

Beginning in 1922 she published a long series of excellent researches on polonium, in which she determined the velocity of its alpha-rays and the distribution of their lengths, and observed their ionizing power, the oscillations in their paths, and the homogeneity of their initial velocity. In 1923 she used an original method to determine the range in air of its alpha-particles.

In the following year Mlles. Curie and C. Chamié measured the half-life period of radon by a method which is very simple in principle. If a *single* tube of radon placed in the ionization chamber yields at time t a given current i, and the time t' is noted at which the same current i is obtained with *two* tubes of radon (the second of which is exactly equivalent to the first), then $t - t' = T$, the half-life period of radon. Since it is impossible to prepare two tubes of radon of exactly the same activity, Mlles. Curie and Chamié applied a correction. Their value for this constant was 3.823 days (*109*).

Mlle. Curie's doctor's dissertation in 1925 was entitled "Investigation regarding the alpha rays of polonium." With the help of various collaborators, including F. Behounek, Mlle. Chamié, J. d'Espine, G. Fournier, N. Yamada, and P. Mercier, she published a number of researches on other radioactive elements, including radium C, radium C′, radon, radium A, and radium E.

In 1926 Mlle. Curie married M. Frédéric Joliot, a young scientist whose tastes, interests, and intellectual attainments are entirely comparable to her own. He was born in Paris in 1900. In 1923 he completed the engineering course at the *Ecole de Physique et de Chimie Industrielle.* Upon the recommendation of his professor, M. Langevin, he became *préparateur* under Mme. Curie and continued his studies at the Sorbonne. He has succeeded M. André Debierne as lecturer at the Faculty of Sciences. So intimate is the collaboration between M. and Mme. Joliot that, when a new discovery is made, they themselves scarcely know in which mind the original concept first arose. In order that the honored name *Curie* might be handed down to their posterity, M. Joliot gladly consented, at the time of his marriage, to add this name to his own. Thus they are known either as M. and Mme. Joliot-Curie or simply as M. and Mme. Joliot. They have two children, a daughter and a son.

Their joint papers on "The numbers of ions produced by alpha rays of radium C′ in air" were published in the *Comptes rendus* in 1928. In the following year they investigated the nature of the absorbable radiation which accompanies the alpha-rays from polonium. In 1930 M. Joliot presented his thesis for the doctorate, which was entitled "The electrochemistry of the radio-elements," and Mme. Joliot continued her study of polonium (*108*).

In speaking of the spontaneous disintegration of the natural radio-elements, the late Mme. Curie pointed out in the biography of her husband that "In many cases, up to the present, no exterior action has shown itself effective in influencing this transformation." This view remains unshaken even to the present day. Near the very close of her life, however, Mme. Curie witnessed the discovery by her own daughter and son-in-law of a wonderful new type of radioactivity, artificially produced (*84*). The transformation of one element into another stable, inactive one had already been accomplished. Lord Rutherford, in 1919, had bombarded nitrogen with swift alpha-particles, or helions, and liberated high-speed protons, and Blackett had shown that the nitrogen nucleus had captured the alpha-particle and that the resulting element was an isotope of oxygen. The nuclear reaction was therefore as follows:

$$_7N^{14} + \underset{\text{helion}}{_2He^4} = {_8O^{17}} + \underset{\text{proton}}{_1H^1}$$

Artificial transmutations into other *stable* elements had also been accomplished.

In 1930 Bothe and Becker observed a very penetrating radiation from beryllium which had been bombarded with helions. M. and Mme. Joliot-Curie found that when they placed paraffin or other hydrogen-containing substances before the window of an ionization chamber, the ionization produced by these new rays increased; for the protons which were ejected from the paraffin by the radiation from the beryllium had a higher ionizing power than the beryllium-radiation itself (*107*). Professor Chadwick has proved that the activity of the beryllium is not merely a hard gamma-radiation, as at first supposed, but that neutrons, or uncharged particles of mass one are also ejected. Each neutron consists of one proton and one negative electron, or negatron, closely bound together; hence its atomic number is zero. The nuclear reaction for the change which occurs when beryllium is bombarded with helions is as follows:

$$_4\mathrm{Be}^9 + {}_2\mathrm{He}^4 = {}_6\mathrm{C}^{12} + \underset{\text{neutron}}{{}_0n^1} + \text{gamma rays}$$

M. and Mme. Joliot showed that boron and lithium, when they are bombarded with alpha-rays from polonium, also emit penetrating radiations (*110*). Their work gave early evidence of the probable existence of the neutron, a hypothesis which has since been fully verified by the researches of Professor James Chadwick, the 1935 Nobel laureate in physics (*142*).

Early in 1934, M. and Mme. Joliot-Curie observed that in some kinds of transmutation, *true radio-elements* are produced which, after their artificial creation, continue for a measurable period of time to emit positive or negative electrons as they disintegrate at last into stable elements (*83*). When M. and Mme. Joliot bombarded boron, aluminum, or magnesium with helions from polonium and photographed the fog-tracks which the ejected electrons made in a Wilson expansion chamber, they noted that, even after the removal of the alpha-ray source, an activity remained which, like that of the natural radioactive elements, decreased in geometrical proportion with the time. The radiations from the bombarded boron and aluminum consisted of positrons; irradiated magnesium, however, gave off a radiation consisting of both positrons and negatrons.

Since the alpha-ray impacts shattered only a minute proportion of the total number of atoms of boron, aluminum, or magnesium, the chemical identification of the products was extremely difficult. These indefatigable workers, however, accomplished even this. Although it would have been impossible to identify the products simply by ordinary chemical means, the Joliots were able to take advantage of the radioactive nature of the products formed. Since they had good reason to believe that the boron atom had captured a helion and ejected a neutron and that the new element was therefore probably an isotope of nitrogen, they heated some bombarded boron nitride with caustic soda and found that the liberated ammonia carried with it the new activity, leaving the residual boron inactive. The nuclear reaction which occurred during the alpha-ray bombardment was therefore as follows:

$$_5\mathrm{B}^{10} + {}_2\mathrm{He}^4 = {}_7\mathrm{N}^{13} + {}_0n^1$$

The new product, which they have named radio-nitrogen, is a hitherto unknown radioactive isotope of ordinary nitrogen. It disintegrates with a half period of fourteen minutes and expulsion of positrons, forming a stable, inactive isotope of carbon:

$${}_{7}\mathrm{N}^{13} = {}_{6}\mathrm{C}^{13} + \underset{\text{positron}}{{}_{1}e^{0}}$$

Since the Joliot-Curies believed that a similar capture of the alpha-particle, with formation of an isotope of phosphorus, had occurred during the bombardment of the aluminum, they treated a piece of irradiated aluminum with hydrochloric acid. The liberated hydrogen carried with it the new activity, probably in the form of phosphine, leaving the aluminum residue inactive. The nuclear reaction which took place during the bombardment was therefore as follows:

$${}_{13}\mathrm{Al}^{27} + {}_{2}\mathrm{He}^{4} = {}_{15}\mathrm{P}^{30} + {}_{0}n^{1}$$

The radio-phosphorus, a hitherto unknown isotope of ordinary phosphorus, disintegrates with a half period of three minutes and fifteen seconds, according to the following reaction:

$${}_{15}\mathrm{P}^{30} = {}_{14}\mathrm{Si}^{30} + {}_{1}e^{0}$$

M. and Mme. Joliot-Curie have shown that the magnesium atom, when similarly bombarded, also captures a helion and emits a neutron, as follows:

$${}_{12}\mathrm{Mg}^{24} + {}_{2}\mathrm{He}^{4} = {}_{14}\mathrm{Si}^{27} + {}_{0}n^{1}$$

The resulting radio-silicon decays with a half life period of two minutes and forty-five seconds, emitting both positrons and negatrons.

Since other projectiles, such as neutrons, protons, and deuterons, have also been used to produce artificial radioactivity, the number of active elements thus created already exceeds by far the number of naturally occurring radio-elements (*111*), (*112*), (*113*). By January, 1940, three hundred and thirty artificial radioactivities had been described; these include isotopes of every known element in the range of atomic numbers 1 to 85 inclusive, as well as isotopes of thorium (atomic number 90) and of uranium (atomic number 92) (*122*). Thus the work of M. and Mme. Joliot-Curie opened up vast avenues of research on the physical, chemical, and radioactive properties of these isotopes and on their therapeutic uses. In 1935 they were awarded the Nobel Prize in chemistry (*94*).

The Trans-uraniums

"Some hold that there remains no further hope of searching out the elements of substances. Poor comfort for those who feel their greatest pleasure in the investigation of natural things! Far mistaken is anyone who endeavours to confine chemistry, this noble science, within such narrow bounds!"—SCHEELE.

Until recently many chemists believed that when all the ninety-two elements from hydrogen to uranium had been found, it would be impossible for anyone ever to discover another one. At present, however, some chemists regard the recently discovered neutron as an element of atomic number zero (*91*), and in the summer of 1934, Professor Enrico Fermi of Rome, one of the world's leading mathematical physicists, made the startling announcement in *Nature* that he had prepared by neutron bombardment of uranium a radioactive substance which he regarded as a new element of atomic number greater than 92 (*82*), (*85*), (*86*).

Although swift alpha-particles can penetrate the nuclei of *light* atoms and produce artificial radioactivity, their positive charge prevents them, because of electrostatic repulsion, from penetrating the more highly charged positive nuclei of *heavy* atoms. Since neutrons are electrically neutral, Professor Fermi selected them as projectiles in his attempts to produce new radioactive substances by bombarding *heavy* elements. Since the alpha-rays from radon are able to liberate neutrons from beryllium, Professor Fermi prepared a sealed glass tube containing radon and pulverized beryllium. Whereas the Joliot-Curies had produced by alpha-ray bombardment a type of artificial radioactivity characterized by the emission of positrons, Professor Fermi produced by neutron bombardment radioactive substances which emit beta-rays (*negative* electrons).

Professor Fermi and his collaborators separated some of these new products chemically and measured their beta-activity with a Geiger-Müller counter. When an element of atomic number Z is bombarded with neutrons, the resulting product may have an atomic number equal to $Z-2$ (aluminum, chlorine, and cobalt give, respectively, radio-sodium, radio-phosphorus, and radio-manganese); $Z-1$ (as in the case of phosphorus, sulfur, iron, and zinc); or (in the case of bromine or iodine) it may be an isotope of the bombarded element. The artificial radioactive substances which the Joliot-Curies had prepared by their original method of alpha-ray bombardment each had an atomic number *greater by two* than that of the bombarded element.

Fermi, Rasetti, and D'Agostino then thought it would be interesting to see how thorium and uranium, which are unstable at best, would behave when bombarded with neutrons. When a disturbance is started in a country which never has been blessed with a stable government, exciting things happen. So it was with thorium and uranium. Both showed a large increase in activity. When Fermi, Rasetti, and D'Agostino bombarded a uranyl nitrate solution from which they had previously removed all disintegration products, they obtained four radioactive substances, with half-life periods of 10 seconds, 40 seconds, 16 minutes, and about 100 minutes, respectively. The bombardment of uranium by neutrons does not appear to have any effect in accelerating its natural rate of disintegration, the increase in activity after bombardment being caused by the formation of these artificial elements, which emit beta rays *(100)*. In the earliest papers on the product with a half-life period of 16 ± 1 minutes it is referred to as "the 13-minute product." In order to separate this product from most of the heaviest elements, Fermi, Rasetti, and D'Agostino added 50 per cent nitric acid to the irradiated uranium solution, treated it with a small amount of a manganese salt, and precipitated the manganese as manganese dioxide by boiling the solution with sodium chlorate. The manganese dioxide precipitate carried down a large percentage of the 16-minute activity.

In attempting to identify the new element, they added to the irradiated uranium nitrate (purified of its disintegration products) various ordinary beta-active elements in sufficient quantity to give about one hundred impulses per minute on the Geiger counter. By showing that the new 16-minute product could be separated from each of these added beta-active elements, they proved that it was not isotopic with any of these known elements. Thus they became convinced that the new substance could not be an isotope of element 82 (lead), 83 (bismuth), 88 (radium), 89 (actinium), 90 (thorium), 91 (uranium X_2), or 92 (uranium). According to Fermi, none of these known beta-active elements are carried down with the manganese dioxide. Moreover, the chemical nature of the 16-minute product is such that it cannot be radon or eka-cesium (element 86 or 87). For this reason, Professor Fermi and his collaborators believed their 16-minute product to be an element with an atomic number of 93, or possibly 94 or 95.

Dr. Aristid V. Grosse of the University of Chicago, who had recently isolated metallic protoactinium and made the first direct determination of its atomic weight, believed for a time that Fermi's new product must be element 91, a new isotope of protoactinium, and that it could not be element 93 *(87)*. When Grosse and Agruss repeated Fermi's experiments, using protoactinium as a radioactive indicator, they found that it, too, was precipitated with the manganese dioxide. Moreover, the fact that rhenium does *not* precipitate with the manganese dioxide led them to believe that Fermi's product could not be element 93 (eka-rhenium), for eka-rhenium ought to resemble rhenium in chemical properties. Grosse also thought that, since none of Fermi's other radio-elements had an atomic number higher than that of the bombarded parent atom, uranium might be expected to yield an element of atomic number 91 rather than 93. Dr. Ida Noddack also pointed out the need for more convincing proof, for when Fermi showed that his 16-minute product could be separated from most of the heaviest elements, he did not consider element 84 (polonium) nor any of the elements preceding lead in the periodic table *(88)*. She found, moreover, that a number of known elements are carried down with the manganese dioxide. Both Dr. Grosse and Dr. Noddack, however, regarded the artificial production of elements heavier than uranium as entirely within the realm of possibility and, indeed, both independently predicted it (*72*), (*87*), (*88*). Basing his deductions (1) on the periodic law and (2) on the Bohr theory, Dr. Grosse predicted the chemical properties of elements 93 and 94 (*87*). According to the periodic law, these elements should resemble, respectively, rhenium and osmium. According to the Bohr theory, however, they ought to resemble uranium or protoactinium and belong to a group of elements which, like the rare earths, are very similar to one another chemically.

At the suggestion of Grosse and Agruss, Professor Fermi precipitated some zirconium phosphate from a solution containing his artificial radioelements. Since Fermi found this precipitate to be inactive, Grosse and Agruss regarded this as the first definite evidence that Fermi's product is not an isotope of element 91.

E. Segrè presented evidence that Professor Fermi's activities of 10 seconds, 16 minutes, and the one with the longer period constitute a series of elements of atomic numbers 92, 93, and 94 and atomic weight 239 (*92*). Professor Fermi was awarded the 1938 Nobel Prize in physics.

In 1935 Hahn and Meitner removed the natural disintegration products from some ammonium uranate, bombarded it with neutrons, and found that the resulting 16-minute and 100-minute substances are not isotopic and that the latter (since its rate of decay does not follow a simple exponential law) must be complex (*90*), (*97*). They described nine transformation products of neutron-bombarded uranium, all of which emit beta rays, and regarded them as: three isotopes of uranium ($Z = 92$) with half-life periods of 10 seconds, 40 seconds, and 23 minutes, respectively; two isotopes of eka-rhenium ($Z = 93$) with periods of 2.2 minutes and 16 minutes; two eka-osmiums ($Z = 94$), 59 minutes and 5.7 hours; one eka-iridium ($Z = 95$), 66 hours; and one eka-platinum ($Z = 96$) with a half-life period of 2.5 hours. With a Geiger beta-ray counter connected to a loud speaker, the late Lord Rutherford on March 19, 1937, demonstrated before the Royal Institution of Great Britain the great beta-ray activity of a uranium preparation which had been freed from uranium-X and exposed to a source of neutrons (*100*).

By irradiating the uranium salt for about an hour, Hahn, Meitner, and Strassmann obtained mainly the supposed elements 93 and 94. To prepare the 66-hour eka-iridium and the 2.5-hour eka-platinum they had to bombard the uranium for days or even for weeks, remove its natural disintegration products, and wait for elements 93 and 94 to break down (*98*), (*99*).

Since only particles with one or two charges were known to be emitted from the bombarded nuclei, the resulting radioactive elements were always believed to have atomic numbers near that of the element bombarded (*119*), (*120*), (*121*). Early in 1939, however, Hahn and Strassmann made the surprising discovery that, when uranium is bombarded with neutrons, its *nucleus* is ruptured, one of the radio-elements thus formed being an isotope of barium (element 56). The existence of atoms heavier than that of uranium therefore remained to be proved. Because of their radioactivity, the so-called trans-uraniums can be detected in vastly smaller concentrations than an inactive element can be. For this reason much has already been learned about their chemical properties (*115*).

Professor Horia Hulubei and Mlle. Yvette Cauchois of Paris have obtained evidence, with their focusing X-ray spectrograph, of the probable existence of element 93 in radioactive minerals (*116*). They obtained their best results with betafites from Madagascar, monazite from Brazil, columbites, and tantalites, especially a French tantalite from Haute-Vienne. This work was done at Paris during a time of great political unrest. At the end of their paper delivered on September 4, 1939, the authors expressed the desire that, "if the existence of this element 93 be confirmed, it be named *sequanium* (*Sq*), in honor of the brave, generous civilization that flourished on the banks of the Seine" (*132*).

E. McMillan and P. H. Abelson found in 1940 that one of the products formed when uranium is bombarded with neutrons is a 2.3-day activity which is a daughter of the 23-minute U^{239} formed when the atom of U^{238} captures a slow neutron. They identified this 2.3-day activity as an isotope, eka-Re^{239}, of element 93, which disintegrates by emission of beta-particles to form element 94 (*122*), (*131*). They found that element 93 bears a closer chemical resemblance to uranium than to its homolog, rhenium. It precipitates, for example, with sodium uranyl acetate and is also thrown down with uranium in alkaline solution and redissolved on addition of ammonium carbonate (*122*), (*144*). It is not precipitated by hydrogen sulfide in dilute acid solution.

Because of the close resemblance between uranium and element 93, these authors believe that uranium may be the first member of a second group of closely related elements similar to the rare earths. The possibility that such a group may exist has been proved mathematically by Dr. Maria Goeppert-Mayer of Columbia University (*133*).

In 1942 F. Strassmann and O. Hahn verified the observations of McMillan and Abelson, separated element 93 by precipitation with sodium uranyl acetate in presence of strong oxidizing agents, studied its chemical properties, and found that the difference between element 93 and uranium is considerably greater than that between lanthanum and cerium, the most easily separable of the rare earths (*141*).

This brief account of the newer and lesser known elements is merely an attempt to present an unprejudiced survey of the literature regarding them. The discovery of an element often proceeds in slow stages: first, the recognition that a certain compound contains something new; years later, perhaps, the observation of new spectral lines; and finally, the concentration of the element, the determination of its atomic weight and its physical and chemical properties, and perhaps its isolation or even its utilization.

Although Dr. Dains and the writer would have liked to publish portraits of all the scientists whose researches have led to the discovery of chemical elements, some of these were unobtainable. Since the discoverers of some of the newer elements preferred not to have their portraits published, we have, of course, respected their wishes, even though we had the portraits.

Conclusion

If the reader has been led through closer acquaintance with the discoverers of the chemical elements to a deeper appreciation of their glorious achievements, the foregoing chapters have not been written in vain. The author gratefully acknowledges the valuable assistance of the late Dr. F. B. Dains, who was untiring in his search for suitable illustrations, and of Mr. Oren Bingham, who made most of the photographic reproductions. The generous coöperation of the library staff and graduate research committee at The University of Kansas, the Edgar Fahs Smith Memorial Library, the former Austro-American Institute of Education, Science Service, and the JOURNAL OF CHEMICAL EDUCATION is deeply appreciated. The publication of valuable illustrations was made possible through the courtesy of the Aluminum Co. of America, the library of the American Philosophical Society, the Army Medical Library, the Bausch and Lomb Optical Co., the Central Scientific Co., Cornell University, the Ecole Supérieure des Mines at Paris, the Fansteel Products Co., the Fisher Scientific Co., the Franklin Institute, Gauthier-Villars et Cie., Harvard University, The Johns Hopkins University, Lehigh University Library, Macmillan and Co., Masson et Cie., the McGraw-Hill Book Co., the Arthur Nemayer Buchdruckerei und Verlag, the Royal Library of Stockholm, the *Scientific American*, the *Scientific Monthly*, and the University of New Hampshire. The author wishes to thank Mr. M. K. Elias and Miss Mary Larson for the Russian and some of the Swedish translations. The kind coöperation of the following persons who assisted in the search for illustrations and other historical material is also acknowledged with pleasure: Dr. Fred Allison, Miss Eva Armstrong, Dr. William H. Barnes, Prof. Gabriel Bertrand, Mr. Carl Björkbom, the late Dr. C. A. Browne, Dr. Otto Brunck, Dr. Fritz Chemnitius, Dr. F. G. Corning, Dr. Dirk Coster, Dr. Tenney L. Davis, Dr. Leonard Dobbin, Dr. A. S. Eve, Dr. P. V. Faragher, the late Miss M. Elizabeth Farson, Dr. A. Fleck, Dr. F. Fiala, Mr. Allyn B. Forbes, M. Freymann, the late Señor A. de Gálvez-Cañero, Dr. Neil E. Gordon, Dr. A. V. Grosse, Dr. W. A. Hamor, Mrs. Gertrude D. Hess, Dr. J. Heyrovský, Mr. Douglas B. Hobbs, Dr. H. N. Holmes, Dr. B. Smith Hopkins, Sir James C. Irvine, Mme. Y. Khouvine, the late Dr. Graham Lusk, Dr.

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Thoughtful readers and reviewers of earlier editions of this book have also given many helpful suggestions.

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(*145*) Maurer, W. and W. Ramm, "Investigation of the 19-minute isotope of molybdenum and its daughter isotope of element 43," *Z. Physik*, **119**, 334–51 (1942).

A LIST OF THE CHEMICAL ELEMENTS

At. No.	Name	Symbol	1943 At. Wt.
0	neutron	n	
1	hydrogen	H	1.0080
2	helium	He	4.003
3	lithium	Li	6.940
4	beryllium	Be	9.02
5	boron	B	10.82
6	carbon	C	12.01
7	nitrogen	N	14.008
8	oxygen	O	16.0000
9	fluorine	F	19.00
10	neon	Ne	20.183
11	sodium	Na	22.997
12	magnesium	Mg	24.32
13	aluminum	Al	26.97
14	silicon	Si	28.06
15	phosphorus	P	30.98
16	sulfur	S	32.06
17	chlorine	Cl	35.457
18	argon	A	39.944
19	potassium	K	39.096
20	calcium	Ca	40.08
21	scandium	Sc	45.10
22	titanium	Ti	47.90
23	vanadium	V	50.95
24	chromium	Cr	52.01
25	manganese	Mn	54.93
26	iron	Fe	55.85
27	cobalt	Co	58.94
28	nickel	Ni	58.69
29	copper	Cu	63.57
30	zinc	Zn	65.38
31	gallium	Ga	69.72
32	germanium	Ge	72.60
33	arsenic	As	74.91
34	selenium	Se	78.96
35	bromine	Br	79.916
36	krypton	Kr	83.7
37	rubidium	Rb	85.48
38	strontium	Sr	87.63
39	yttrium	Y	88.92
40	zirconium	Zr	91.22
41	columbium	Cb	92.91
42	molybdenum	Mo	95.95
43			
44	ruthenium	Ru	101.7
45	rhodium	Rh	102.91
46	palladium	Pd	106.7
47	silver	Ag	107.880

At. No.	Name	Symbol	1943 At.
48	cadmium	Cd	112.41
49	indium	In	114.76
50	tin	Sn	118.70
51	antimony	Sb	121.76
52	tellurium	Te	127.61
53	iodine	I	126.92
54	xenon	Xe	131.3
55	cesium	Cs	132.91
56	barium	Ba	137.36
57	lanthanum	La	138.92
58	cerium	Ce	140.13
59	praseodymium	Pr	140.92
60	neodymium	Nd	144.27
61	illinium	Il	
62	samarium	Sm	150.43
63	europium	Eu	152.0
64	gadolinium	Gd	156.9
65	terbium	Tb	159.2
66	dysprosium	Dy	162.46
67	holmium	Ho	164.94
68	erbium	Er	167.2
69	thulium	Tm	169.4
70	ytterbium	Yb	173.04
71	lutecium	Lu	174.99
72	hafnium	Hf	178.6
73	tantalum	Ta	180.88
74	tungsten	W	183.92
75	rhenium	Re	186.31
76	osmium	Os	190.2
77	iridium	Ir	193.1
78	platinum	Pt	195.23
79	gold	Au	197.2
80	mercury	Hg	200.61
81	thallium	Tl	204.39
82	lead	Pb	207.21
83	bismuth	Bi	209.00
84	polonium	Po	210.0
85			
86	radon	Rn	222
87			
88	radium	Ra	226.05
89	actinium	Ac	
90	thorium	Th	232.12
91	protoactinium	Pa	231
92	uranium	U	238.07
93			
94			

Little is known about elements 43, 61, 85, 87, 93, and 94. The names and symbols proposed for them are given in the preceding pages of Chapter XXVII. The International Committee on Atomic Weights gives no report for these elements nor for actinium.

CHRONOLOGY

Sixteenth Century

1524	Hernando Cortes sees coins made of tin from Taxco in use in Mexico.
1541	Francisco Vazquez de Coronado observes a copper ornament worn by an Indian chief, in what is now the southwestern part of the United States.
1570	Pedro Fernándes de Velasco demonstrates his cold amalgamation process for the recovery of silver from the ores of Mount Potosí (Bolivia).
1590	The Chinese encyclopedia of materia medica, the Pen Ts'ao Kan-Mu, describes the uses of arsenic.
1590	Father José de Acosta describes the metallurgy of silver and mercury in the New World.

Seventeenth Century

1602	John Brereton describes the copper artifacts of the Indians of Virginia.
1604	The "Triumphal Chariot of Antimony" by Pseudo-Basilius Valentinus is published.
Jan. 25, 1627	Birth of Robert Boyle in Ireland. Independent discoverer of phosphorus.
1630	Birth of Johann Kunckel, early writer on phosphorus.
1637	A Chinese book entitled "Tien kong kai ou" describes the metallurgy and uses of zinc.
1640	Father A. A. Barba of Potosí publishes the first treatise on American metallurgy.
1641	Birth of Dr. John Mayow in London. Author of an early theory of combustion.
Nov. 17, 1645	Birth of Nicolas Lémery at Rouen
1649	Schroeder describes two methods of preparing metallic arsenic.
1665	Robert Hooke gives a theory of combustion in his book "Micrographia."
1669	The alchemist Brand of Hamburg discovers phosphorus.
1670	Heinrich Schwanhard etches glass with a mixture of fluorospar and a concentrated acid.
1671	Robert Boyle prepares hydrogen ("inflammable solution of Mars") by dissolving iron in dilute hydrochloric or sulfuric acid.
1674	Dr. John Mayow recognizes that the air has two constituents.
1679	Death of Dr. Mayow.
1683	Johann Bohn distinguishes between "cubic saltpeter" (sodium nitrate) and ordinary "prismatic" saltpeter.

1688	Bernard Albinus (Weiss) mentions the presence of phosphorus in the ash of mustard and cress.
1691	Death of Robert Boyle.
June 26, or July 21, 1694	Birth of Georg Brandt, the discoverer of cobalt, at Riddarhytta, Vestmanland, Sweden.
1695	Nehemiah Grew publishes a dissertation on Epsom salt.
1700	Lémery describes hydrogen.

Eighteenth Century

1701	A posthumous edition of Turquet de Mayerne mentions the inflammability of hydrogen.
1702	Death of Kunckel.
1702	Wilhelm Homberg prepares "sedative salt" (boric acid).
1702	G. E. Stahl distinguishes between the natural and the artificial alkali (soda and potash).
1707	Nicolas Lémery publishes his "Treatise on Antimony."
Mar. 3, 1709	Birth of Andreas Sigismund Marggraf at Berlin.
June 19, 1715	Death of Nicolas Lémery.
Dec. 23, 1722	Birth of Axel Fredrik Cronstedt, the discoverer of nickel, in Södermanland, Sweden.
Oct. 10, 1731	Birth of Henry Cavendish at Nice.
Mar. 13, 1733 (old style)	Birth of Joseph Priestley at Fieldhead, Yorkshire, near Leeds.
1735	Birth of Torbern Bergman.
1736	H.-L. Du Hamel du Monceau demonstrates that the mineral alkali (soda) is a constituent of common salt, of Glauber's salt, and of borax, and prepares sodium carbonate from salt.
1737	Hellot prepares a button of metallic bismuth and makes public the secret process for preparing phosphorus.
1737–38	Georg Brandt isolates cobalt.
1740	J. H. Pott states that pyrolusite contains the calx of a new metal.
July 1, 1740	Birth of Müller von Reichenstein, the discoverer of tellurium, at Nagyszeben, Transylvania.
1740–41	Charles Wood finds in Jamaica some platinum which has come from Carthagena, New Spain.
1742	Anton von Swab distills zinc from calamine.
Dec. 9, 1742	Birth of Carl Wilhelm Scheele at Stralsund, Swedish Pomerania.
Aug. 26, 1743	Birth of Lavoisier in Paris.
Dec. 1, 1743	Birth of Martin Heinrich Klaproth at Wernigerode in the Harz. One of the first to investigate uranium, titanium, and cerium.

Aug. 19, 1745	Birth of Johan Gottlieb Gahn, the discoverer of manganese, at Voxna, South Helsingland, Sweden.
1746	Marggraf prepares metallic zinc by reduction of calamine.
Oct. 2, 1746	Birth of Peter Jacob Hjelm, the discoverer of molybdenum, at Sunnerbo Härad, Sweden.
1748	Don Antonio de Ulloa describes platinum.
Nov. 3, 1749	Birth of Daniel Rutherford, the discoverer of nitrogen, at Edinburgh.
1750	Dr. William Brownrigg describes platinum.
1751	Cronstedt isolates nickel.
1752	H. T. Scheffer fuses platinum with the aid of arsenic.
1753	Claude-François Geoffroy's research on "The Chemical Analysis of Bismuth" is published.
1754	Marggraf prepares and characterizes alumina.
Oct. 11, 1755	Birth of Don Fausto d'Elhuyar at Logroño, Spain. With his brother, Don Juan José, he isolated tungsten.
1755	Dr. Joseph Black of Edinburgh recognizes magnesia alba to be distinct from lime.
1758–59	Marggraf independently recognizes the distinction between magnesia and lime, and uses flame tests to distinguish between the nitrates of sodium and potassium.
June 5, 1760	Birth of Johan Gadolin, the discoverer of yttria, at Åbo, Finland.
Nov. 30, 1761	Birth of Smithson Tennant, the discoverer of osmium and iridium, at Wensleydale, Yorkshire.
Dec. 25, 1761	Birth of the Reverend William Gregor, the discoverer of titanium, in Trewarthenick, Cornwall.
May 16, 1763	Birth of N.-L. Vauquelin, the discoverer of chromium and beryllium, at St. André des Berteaux.
Nov. 10, 1764	Birth of A. M. del Río, discoverer of vanadium (erythronium), in Madrid.
Jan. 2, 1765	Birth of Charles Hatchett, the discoverer of columbium (niobium), in London.
Aug. 19, 1765	Death of Cronstedt in Säters parish, near Stockholm.
Aug. 6, 1766	Birth of Dr. William Hyde Wollaston, the discoverer of palladium and rhodium, at East Dereham, Norfolkshire.
Dec., 1766	Birth of Wilhelm Hisinger, the discoverer of the earth ceria. Berzelius, Hisinger, and Klaproth all investigated this earth, the latter independently.
Jan. 16, 1767	Birth of Anders Gustaf Ekeberg, the discoverer of tantalum, at Stockholm.
Apr. 29, 1768	Death of Georg Brandt at Stockholm.

1769	Scheele and Gahn isolate phosphorus from bones.
1770	P. S. Pallas describes the "red lead of Siberia" (crocoite), in which Vauquelin later discovered chromium. This mineral had been analyzed four years earlier by J. G. Lehmann.
1771	Scheele describes hydrofluoric acid.
1772	Daniel Rutherford discovers nitrogen. (Scheele, Priestley, and Cavendish discover it independently at about the same time.)
1772–82	Baron Carl von Sickingen devises a process for making platinum malleable.
Apr., 1774	Pierre Bayen prepares oxygen by heating mercuric oxide.
1774	Scheele publishes his famous treatise "Concerning Manganese and its Properties," which led to the discovery of three elements: manganese, barium, and chlorine.
Aug. 1, 1774	Priestley prepares oxygen. (Scheele prepared it before this, but his results were not published until 1777.)
1774	Gahn isolates manganese.
1775	Johan Arvidsson Afzelius publishes his doctor's dissertation defending Bergman's belief in the elementary nature of nickel. (He sometimes signed his name Johan Afzelius Arvidsson.)
Aug. 2, 1776	Birth of Friedrich Stromeyer, the discoverer of cadmium, at Göttingen.
Feb. 8, 1777	Birth of Bernard Courtois, the discoverer of iodine, at Dijon.
1777	Lavoisier overthrows the phlogiston theory and demonstrates the true nature of combustion.
May 4, 1777	Birth of Louis-Jacques Thenard.
Aug. 14, 1777	Birth of Hans Christian Oersted.
1778	Scheele distinguishes between graphite and the ore then known as "molybdenum."
Dec. 6, 1778	Birth of Gay-Lussac at Saint-Léonard.
Dec. 17, 1778	Birth of Sir Humphry Davy at Penzance, Cornwall.
1779	Scheele distinguishes between lime and baryta.
Aug. 20, 1779	Birth of Berzelius at Wäfversunda, Sweden.
1780	Birth of J. W. Döbereiner, the discoverer of the "triads."
1781	Scheele discovers tungstic acid.
1781	Hjelm isolates molybdenum.
Aug. 7, 1782	Death of Marggraf.
1783	Discovery of tellurium by Müller von Reichenstein.
1783	Discovery of tungsten by the d'Elhuyar brothers.

1783	P.-F. Chabaneau patents a process for making platinum malleable.
1784	Death of Torbern Bergman.
1785	R. E. Raspe shows that tungsten hardens steel.
May 21, 1786	Death of Scheele.
June 2, 1787	Birth of Nils Gabriel Sefström, the rediscoverer of vanadium, in Ilsbo Socken, Sweden. Although vanadium is now known to be identical with del Río's "erythronium," the latter chemist did not distinguish clearly between chromium and the new element.
1789	Klaproth observes uranium in pitchblende, but does not isolate it. In the same year he discovers the earth zirconia.
1790	Hjelm publishes his first paper on molybdenum. He had isolated it as early as 1781.
1790	Adair Crawford recognizes strontia as a new earth.
1791	The Rev. William Gregor discovers the oxide of a new metal, titanium.
Jan. 12, 1792	Birth of Johan August Arfwedson, the discoverer of lithium, at Skagerholms-Bruk, Skaraborgs Län.
May 8, 1794	Death of Lavoisier on the guillotine.
1794	Gadolin discovers the earth yttria.
May 29, 1794	Birth of A.-A.-B. Bussy at Marseilles. He obtained magnesium in coherent form.
1795	Klaproth re-discovers titanium, but does not succeed in isolating it.
Jan. 23, 1796	Birth of Karl Karlovich Klaus, the discoverer of ruthenium, at Dorpat, Esthonia.
1797	Smithson Tennant proves that the diamond consists solely of carbon.
Sept. 10, 1797	Birth of Carl Gustav Mosander, the discoverer of lanthanum and didymium, at Kalmar, Sweden.
Feb., 1798	Vauquelin recognizes beryllium (glucinum) and isolates chromium. Beryllium was first isolated in 1828 by Wöhler.
Jan. 25, 1798	Klaproth brings Müller von Reichenstein's discovery of tellurium to the attention of German chemists.
Feb. 19, 1799	Birth of Ferdinand Reich, the discoverer of indium, at Bernburg.
July 31, 1800	Birth of Friedrich Wöhler at Eschersheim, Germany.
1800	J. B. de Andrada describes petalite and spodumene, minerals in which J. A. Arfwedson afterward discovered lithium.

Nineteenth Century

1801	Robert Hare fuses platinum. Two years later he volatilizes it.
1801	Del Río recognizes the presence of a new metal "erythronium" (vanadium) in a lead ore from Zimapán, Mexico. He afterward confuses it with chromium.
1801	Hatchett observes columbium (niobium) in an ore from New England.
1802	Ekeberg discovers the earth tantala.
Sept. 30, 1802	Birth of A.-J. Balard, the discoverer of bromine, at Montpellier.
Mar. 17, 1803	Birth of Carl Löwig, independent discoverer of bromine.
1803	Klaproth, Berzelius, and Hisinger analyze cerite and discover the earth ceria.
1803	Wollaston discovers palladium and rhodium.
Feb. 6, 1804	Death of Priestley at Northumberland, Pa.
1804	Smithson Tennant discovers osmium and iridium.
Oct. 6, 1807	Davy isolates potassium. A few days later he isolates sodium.
1808	Davy isolates barium, strontium, calcium, and magnesium.
1808	Gay-Lussac and Thenard isolate boron. Davy isolates it independently.
1809	Gay-Lussac and Thenard prove that sulfur is an element.
1809	Dr. Wollaston makes the erroneous conclusion that tantalum and columbium are identical.
Feb. 24, 1810	Death of Cavendish.
Nov. 15, 1810	Davy announces his proof of the elementary nature of chlorine to the Royal Society.
1811	Courtois discovers iodine.
Mar. 24, 1811	Birth of Eugène-Melchior-Peligot, the first to isolate uranium.
Mar. 31, 1811	Birth of Robert Bunsen at Göttingen.
Feb. 11, 1813	Death of Ekeberg at Upsala.
Oct. 7, 1813	Death of Hjelm at Stockholm.
1813	Clément confirms the discovery of iodine by Courtois.
1814	Fraunhofer discovers the dark lines in the sun's spectrum.
1814	Gay-Lussac publishes his classical research on iodine
Feb. 22, 1815	Death of Tennant at Boulogne-sur-Mer.
Jan. 1, 1817	Death of Klaproth at Berlin.
Apr. 24, 1817	Birth of Jean Galissard de Marignac, the discoverer of ytterbia and gadolinia, at Geneva, Switzerland.

June 11 (or July 11), 1817	Death of William Gregor.
1817	Arfwedson discovers lithium.
1817	Stromeyer discovers cadmium.
1818	Berzelius discovers selenium.
Mar. 11, 1818	Birth of Henri Sainte-Claire Deville on the island of St. Thomas in the Antilles.
Dec. 8, 1818	Death of Gahn at Stockholm.
Dec. 15, 1819	Death of Daniel Rutherford.
1820	Birth of Beguyer de Chancourtois, the discoverer of the "telluric screw."
July 15, 1820	Birth of Claude-August Lamy at Néry, France. He prepared thallium in the metallic state.
1822	Discovery of platinum in the Urals.
1824	Berzelius isolates amorphous silicon.
Mar. 12, 1824	Birth of Gustav Kirchhoff at Königsberg.
Nov. 21, 1824	Birth of Hieronymus Theodor Richter, the first to observe the indigo line of indium.
1824	Berzelius isolates impure zirconium.
1825	Oersted isolates impure aluminum.
Oct. 12, 1825 (1826?)	Death of Müller von Reichenstein at Vienna.
1825	Berzelius prepares impure amorphous titanium.
1825	Carl Löwig isolates bromine.
1826	Balard isolates bromine. His results were published before those of Löwig.
1827	Wöhler isolates aluminum.
1828	Wöhler isolates beryllium. Bussy isolates it independently.
Dec. 22, 1828	Death of Dr. Wollaston in London. His specifications for making platinum malleable were circulated at the same time as the news of his death.
1829	Berzelius separates the earth thoria from thorite.
1829	Döbereiner observes the triads.
May 29, 1829	Death of Davy at Geneva, Switzerland.
Nov. 14, 1829	Death of Vauquelin at the Château des Berteaux.
1830	Sefström rediscovers vanadium.
Aug. 19, 1830	Birth of Lothar Meyer at Varel on the Jade.
1831	Bussy obtains magnesium in compact form. (Davy had isolated it in 1808.)
June 17, 1832	Birth of Sir William Crookes.
Jan. 6, 1833	Death of Don Fausto d'Elhuyar at Madrid.
Jan. 7, 1833	Birth of Sir Henry E. Roscoe, the first to liberate metallic vanadium.

Feb. 8 (Jan. 27), 1834	Birth of Mendeléeff at Tobolsk, Siberia.
Aug. 18, 1835	Death of Stromeyer at Göttingen.
1837	Birth of J. A. R. Newlands, the discoverer of the law of octaves.
Apr. 18, 1838	Birth of Lecoq de Boisbaudran at Cognac.
Sept. 27, 1838	Death of Courtois in Paris.
Dec. 26, 1838	Birth of Clemens Winkler, the discoverer of germanium, at Freiberg.
1839	Mosander discovers lanthana.
Feb. 10, 1840	Birth of Per Theodor Cleve, the discoverer of thulium, at Stockholm.
May 27, 1840	Birth of Lars Fredrik Nilson, the discoverer of scandium, in Östergötland, Sweden.
1841	Peligot isolates uranium.
1841	Mosander discovers didymia.
Oct. 28, 1841	Death of J. A. Arfwedson at his Hedensö estate.
Nov. 12, 1842	Birth of Robert John Strutt, Lord Rayleigh, at Terling, England.
1843	Mosander separates terbia and erbia from gadolinite.
1844	Klaus discovers ruthenium.
Nov. 30, 1845	Death of Sefström at Stockholm.
Mar. 10, 1847	Death of Hatchett at Chelsea.
Aug. 7, 1848	Death of Berzelius at Stockholm.
Mar. 23, 1849	Death of del Río in Mexico.
Mar. 24, 1849	Death of Döbereiner.
May 9, 1850	Death of Gay-Lussac in Paris.
Mar. 9, 1851	Death of Oersted.
Jan. 1, 1852	Birth of E.-A. Demarçay, the discoverer of europium.
June 28, 1852	Death of Hisinger.
Aug. 15, 1852	Death of Gadolin.
Sept. 28, 1852	Birth of Henri Moissan in Paris.
Oct. 2, 1852	Birth of Sir William Ramsay at Glasgow.
1854	David Alter observes that each element has a characteristic spectrum.
1854	Henri Sainte-Claire Deville perfects an industrial process for aluminum and prepares the first crystalline silicon.
June 21, 1857	Death of Thenard.
Sept. 1, 1858	Birth of Karl Auer, Baron von Welsbach.
Oct. 15, 1858	Death of Mosander.
May 15, 1859	Birth of Pierre Curie.
1859	Invention of the spectroscope by Kirchhoff and Bunsen.

May 10, 1860	Bunsen and Kirchhoff announce the discovery of cesium.
Feb. 23, 1861	Bunsen and Kirchhoff announce the discovery of rubidium.
Spring, 1861	Crookes observes the green line of thallium.
Spring, 1862	Lamy prepares an ingot of metallic thallium.
1862	Beguyer de Chancourtois draws his "telluric screw."
1863	Birth of P.-L.-T. Héroult and of Charles Martin Hall, independent discoverers of the electrolytic process for preparing metallic aluminum.
Summer, 1863	Reich and Richter discover indium.
1864	Newlands and Lothar Meyer independently arrange the elements in series and families.
Mar. 24, 1864	Death of Klaus.
Nov. 7, 1867	Birth of Marie Sklodowska (Mme. Curie) at Warsaw, Poland.
1868	Janssen and Lockyer independently observe the D line of helium in the sun's chromosphere.
July 9, 1868	Birth of N. A. Langlet.
June 16, 1869	Roscoe announces the isolation of vanadium.
1869	Lothar Meyer and Mendeléeff independently discover the periodic system.
1870	Birth of B. B. Boltwood, the discoverer of ionium.
Jan. 24, 1872	Birth of Morris William Travers at London.
April 12, 1872	Birth of Georges Urbain, the discoverer of lutecium.
Sept. 1, 1873	Birth of B. Smith Hopkins, the discoverer of illinium, at Owosso, Michigan. This element was discovered independently by the American chemists, Cork, James, and Fogg.
Aug. 27, 1875	Boisbaudran discovers gallium, the first element to be discovered with the aid of the spark spectrum.
Oct., 1875	Lewis Reeve Gibbes presents his "Synoptical Table of the Elements."
Mar. 30, 1876	Death of Balard at Paris.
1878	Marignac separates ytterbia from erbia.
Mar. 20, 1878	Death of Lamy at Paris.
1879	Boisbaudran discovers samaria.
1879	Nilson discovers scandium (eka-boron).
1879	Cleve discovers holmia and thulia. The former had been discovered independently by Soret in 1878.
Apr. 27, 1880	Birth of Charles James near Northampton, England.
Jan. 1, 1881	Death of Henri Sainte-Claire Deville at Boulogne-sur-Seine.
Feb. 1, 1882	Death of Bussy at Paris.

Apr. 27, 1882	Death of Ferdinand Reich.
Oct. 9, 1882	Death of Wöhler.
1885	Birth of Georg von Hevesy in Budapest. Co-discoverer with Dirk Coster of the element hafnium.
June 18, 1885	Auer von Welsbach announces his separation of didymia into praseodymia and neodymia.
1886	Death of Beguyer de Chancourtois.
1886	Boisbaudran discovers dysprosia and gadolinia, but finds that the latter is identical with an oxide discovered by Marignac in 1880.
Feb. 6, 1886	Winkler discovers germanium.
Feb. 23, 1886	Charles Martin Hall produces electrolytic aluminum. Dr. Héroult made the same discovery independently at about the same time.
June 26, 1886	Moissan isolates fluorine.
Oct. 17, 1887	Death of Kirchhoff.
Nov. 23, 1887	Birth of Moseley at Weymouth, England.
Apr. 15, 1890	Death of Peligot in Paris.
1892	Lord Rayleigh finds that atmospheric nitrogen is heavier than nitrogen from the decomposition of ammonia.
1894	Ramsay and Rayleigh announce the discovery of argon.
Apr. 15, 1894	Death of Marignac.
1895	Ramsay and Cleve independently discover helium.
Apr. 11, 1895	Death of Lothar Meyer.
May 30, 1898	Ramsay and Travers discover krypton.
June, 1898	Ramsay and Travers discover neon.
July 12, 1898	Ramsay and Travers discover xenon.
July, 1898	Mme. Curie discovers polonium.
July 29, 1898	Death of J. A. R. Newlands.
Sept. 25, 1898	Death of Hieronymus Richter.
Dec., 1898	M. and Mme. Curie discover radium.
1898	Mme. Curie and G. C. Schmidt independently discover the radioactivity of thorium.
May 14, 1899	Death of Nilson.
Aug. 16, 1899	Death of Bunsen.
1899	Debierne discovers actinium.
1900	Dorn discovers radon (radium emanation).
1900	Sir William Crookes discovers uranium X_1.

Twentieth Century

1901	Demarçay discovers europium.
1902	Rutherford and Soddy discover thorium X.

1904	B. B. Boltwood, H. N. McCoy, and R. J. Strutt prove independently that radium is produced by spontaneous transmutation of uranium.
Oct. 8, 1904	Death of Winkler.
1904	Death of Demarçay at Paris.
1904–5	Giesel and Godlewski independently discover actinium X.
1905	Hahn discovers radiothorium and mesothorium I.
June 18, 1905	Death of Cleve at Upsala.
1906	Hahn discovers radioactinium.
Apr. 19, 1906	Death of Pierre Curie.
1907	H. N. McCoy and W. H. Ross clearly recognize the existence of isotopes, or chemically inseparable elements.
1907	Boltwood discovers ionium. This element was independently discovered by Hahn and Marckwald
Feb. 2, 1907	Death of Mendeléeff.
Feb. 20, 1907	Death of Moissan.
1907	Urbain discovers lutecium.
1907	Von Bolton prepares a columbium regulus.
1909	E. Weintraub prepares pure fused boron.
1910	Mme. Curie and M. Debierne isolate radium metal.
1910	M. A. Hunter prepares titanium 99.9 per cent pure.
1911	Antonoff discovers uranium Y.
May 28, 1912	Death of Boisbaudran.
1913	Fajans and Göhring discover uranium X_2 (element 91, eka-tantalum).
Dec., 1913, and Apr., 1914	Moseley publishes his papers on "The High Frequency Spectra of the Elements."
1914	T. W. Richards discovers a radioactive isotope of lead.
1914	Death of P.-L.-T. Héroult and C. M. Hall.
Aug. 10, 1915	Moseley killed at the Dardanelles.
Dec. 18, 1915	Death of Sir Henry E. Roscoe.
July 23, 1916	Death of Ramsay.
1917	Hahn and Meitner discover protoactinium. Soddy and Cranston discover it independently.
Apr. 4, 1919	Death of Sir William Crookes.
June 30, 1919	Death of Lord Rayleigh.
1921	Hahn discovers uranium Z.
Jan., 1923	Coster and Hevesy discover hafnium (element 72).
June, 1925	Noddack, Tacke, and Berg announce masurium and rhenium (elements 43 and 75).
June, 1926	Hopkins, Harris, and Yntema announce the discovery of illinium (element 61).

July 1, 1926	Death of F. F. Jewett in Honolulu.
July, 1926	Rolla and Fernandes announce the discovery of element 61, their preliminary results having been deposited in June, 1924, as a sealed package with the *Reale Accademia dei Lincei.*
1927	Death of Boltwood.
Dec. 10, 1928	Death of Charles James in Boston.
Aug. 4, 1929	Death of Auer von Welsbach at Welsbach Castle in Carinthia.
1930	Allison and Murphy announce the discovery of element 87 (virginium), as a result of their magneto-optic method of analysis.
May, 1931	Allison, Murphy, Bishop, and Sommer announce the discovery of element 85 (alabamine).
Oct., 1931	Papish and Wainer obtain spectroscopic evidence of element 87.
1932	H. C. Urey, F. G. Brickwedde, and G. M. Murphy discover the hydrogen isotope of mass 2.
1932	J. Chadwick and M. and Mme. Joliot-Curie demonstrate the existence of the neutron, which W. D. Harkins regards as the atom of an element "neuton" of atomic number zero.
1934	Colin G. Fink and P. Deren perfect a process for electro-plating rhenium.
Jan. 15, 1934	M. and Mme. Joliot-Curie produce artificial radioactive elements by α-ray bombardment of light elements.
June, 1934	Enrico Fermi produces by neutron bombardment of uranium radioactive substances which may have atomic numbers greater than 92.
July 4, 1934	Death of Mme. Curie.
Sept., 1934	A. V. Grosse liberates metallic protoactinium.
1935	Hahn and Meitner confirm Fermi's discovery of the so-called trans-uraniums.
March 30, 1936	Death of N. A. Langlet.
Oct. 19, 1937	Death of Lord Rutherford.
1937	Perrier, Segrè, and Cacciapuoti prepare radioactive isotopes of element 43.
1937	Horia Hulubei reports the discovery of element 87 with his curved crystal focusing X-ray spectrograph.
Nov. 5, 1938	Death of Georges Urbain.
1938–39	H. Hulubei and Mlle. Cauchois report the probable existence of element 93 in radioactive minerals.
1939	Mlle. Marguerite Perey prepares element 87 (actinium K), which is formed by the alpha-disintegration of a small percentage of the atoms of actinium.
1939	Hahn and Strassmann split the nucleus of the uranium atom.

1940	Corson, MacKenzie, and Segrè prepare element 85 by bombarding bismuth with helions. W. Minder and Hulubei and Cauchois independently give evidence for the existence of element 85 in the decay products of radon.
1940	McMillan and Abelson prepare element 93 by bombarding uranium with neutrons, and find that it bears a closer resemblance to uranium than to rhenium.
Jan. 17, 1941	Death of Sven Otto Pettersson at Göteborg.
Dec. 2, 1941	Death of Thomas H. Norton.

APPENDIX

Dr. Bohuslav Brauner and the Splitting of Didymium

The following literal translation of a postcard from the late Professor Bohuslav Brauner to the late Dr. Max Speter is published by kind permission of Dr. Speter. It was written in reply to a question as to whether or not Brauner and the late Auer von Welsbach were students under Mendeléeff. Dr. Brauner was about seventy-eight years old when he wrote this card.

Prague, Weinberge, Polska 14.
May 18, 1933

ESTEEMED COLLEAGUE:

It pleased me that you welcomed my reprints. I am a genuine Praguer. I was with Master Mendelejew in 1882, but did not hear that *he* [Auer von Welsbach] had been with him. M. wished to work with me, on H_2:O in fact, yet I could not remain! M. visited me in Prague, and I later went to see him in Petersburg. I remember well that you once visited me in Prague. It is interesting that A. W. [Auer von Welsbach] often did the same as I. I learned from Bunsen in 1878–9 how to work with the rare earths; he did the same in 1883, but when I was visiting in the same place, he [A. v. W.?] did not present himself. I found in 1882, through study of the decomposition products of the old didymium, that it can be split into two earths (absorption spectra) and published a note on it in the Wiener Anzeiger. He published his work on praseodymium and neodymium in 1885.

Cordially yours,
PROF. BRAUNER

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Names of persons are printed in capital and small capital letters, page numbers for the portraits are in italics, and page numbers for the biographical sketches in boldface type.