1. Out of alchemy

> While thus employed, Gerard was busy about the seated corpse and to his amazement, Denys saw a luminous glow spreading rapidly over the white face. Gerard blew out the candle. And on this the corpse's face shone still more like a glowworm's head. Denys shook in his shoes and his teeth chattered.
>
> 'What in Heaven's name is this?' he whispered.
>
> 'Hush! 'tis but phosphorus. But 'twill serve.'
>
> In half a minute Gerard's brush made the dead head a sight to strike any man with dismay. He put his art to a strange use and one unparalleled perhaps in the history of mankind. He illuminated his dead enemy's face to frighten his living foe; the staring eyes he made globes of fire; the teeth he left white . . . but the palate and tongue he tipped with fire . . . and on the brow he wrote in burning letters LA MORT.

Charles Reade's best-selling novel, *The Cloister and the Hearth*, from which this extract is taken, was published in 1861. The story recounts the adventures of two friends, Gerard and Denys, as they romp their way across Europe in the middle years of the fifteenth century. The book was much admired, not only for being a good read, but for its attention to historical detail, although the author got it very wrong when it came to phosphorus. This element was unknown in the Middle Ages, even if it was an everyday item when Reade wrote his book.

The time-slip is partly excusable because the origin of phosphorus was shrouded in mystery. It had even been suggested that it was known in the days of ancient Rome, and it may well be that the secret of its manufacture was discovered – and lost – more than once down the centuries. This we can attribute to the paranoid secrecy of the alchemists as they searched endlessly for the philosopher's stone, the mythical compound that would turn base metals like lead into gold. It was one of their number who finally revealed phosphorus to the world, but that was 200 years after the time of Gerard and Denys.

Uncertainty still surrounds the date on which phosphorus was first made. We can be fairly sure the place was Hamburg in Germany, and that the year was probably 1669, but the month and day are not recorded, though it must have been night-time. The alchemist who made the discovery stumbled upon a material the like of which had never been seen. Unwittingly he unleashed upon an unsuspecting world one of the most dangerous materials ever to have been made.

On that dark night our lone alchemist was having no luck with his latest experiments to find the philosopher's stone. Like many before him he had been investigating the golden stream, urine, and he was heating the residues from this which he had boiled down to a dry solid. He stoked his small furnace with more charcoal and pumped the bellows until his retort glowed red hot. Suddenly something strange began to happen. Glowing fumes filled the vessel and from the end of the retort dripped a shining liquid that burst into flames. Its pungent, garlic-like smell filled his chamber. When he caught the liquid in a glass vessel and stoppered it he saw that it solidified but continued to gleam with an eerie pale-green light and waves of flame seemed to lick its surface. Fascinated, he watched it more closely, expecting this curious cold fire to go out, but it continued to shine undiminished hour after hour. Here was magic indeed. Here was phosphorus.

That Hamburg alchemist was Hennig Brandt, a rather pompous man who insisted on being called *Herr Doktor* Brandt.

His first thought was that he had at last found what he had been searching for. Surely this wondrous new material was the philosopher's stone? If so, he had better keep the secret to himself while he made his fortune. And so for six long years he hid his discovery from the world, until his wealth was all but spent. Magical though it was, his phosphorus stubbornly refused to bring the riches of which he dreamed. Today we know his was a vain hope, but the luminescent material he had made was to create great wealth for a few in the centuries ahead. It was to create untold misery for many more.

Frustrated by his inability to make gold with phosphorus, Brandt finally revealed its existence to friends and neighbours and soon it was the talk of Hamburg. While Brandt enjoyed the fame it brought him he still kept secret the method of its making, although he let it be known that it was of human origin. A few of those he showed it to became fascinated by it and, guessing that it must derive from urine, tried to make it for themselves. They sometimes succeeded and when they wrote about it they were less coy about how it was made, which is why its discovery came to be attributed to others. Brandt never published an account of his discovery and he soon faded into obscurity. None of his papers has survived, but, even if they had, it is most unlikely that we would be able to interpret their alchemical symbols and arcane language. Those who dabbled in that ancient lore guarded their secrets well, fearful lest their work – or their chicanery – should be betrayed to the princes, kings and emperors who funded them. Brandt, who was arguably the most successful of them all, was funded by his first and second wives.

There is no recorded date of Brandt's birth, although it was probably in the 1620s, nor are there records of the year he married his first wife, or of when she died. We know they had at least two children. Then he married Margaretha, a rich widow who already had a son by her first marriage, and this stepson helped Brandt in his laboratory. It was her wealth that enabled the alchemist to continue his search for the philosopher's stone and thereby discover phosphorus.

The little we do know about Brandt comes from letters written by Margaretha and from comments of those he had dealings with. We know he lived in the Michaelisplatz part of Hamburg at the time he made his discovery and was probably a native of that city. He was said by some to be a man of humble birth who in his youth had been apprenticed to a glass-maker, a trade which would stand him in good stead when he turned his attention to alchemy because it enabled him to produce the high temperatures necessary to generate phosphorus. However, in one letter written by Margaretha in November 1678 she said her husband was of high social standing, which might well have been true.

In his early days Brandt had been a soldier when such men were in great demand* and even held the rank of a junior officer, which perhaps indicated that he was from a respectable family. His first wife came with a substantial dowry and it was her money that allowed him to take up alchemy when he left the army. By the time she died he had spent most of it on his fruitless search, but his depleted coffers were soon replenished by his second marriage.

Those who knew Brandt have also left a few clues to his character. He was said to be of whimsical temperament and secretive, but Ambrose Godfrey, who sought him out around 1680, hoping to discover how phosphorus was made, referred to him as 'old honest Brandt of Hamburg', although others doubted

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* This was the time of the so-called Thirty Years' War (1618–48), which raged across Europe and pitted Catholics against Protestants, Austria against the German states, the German states against one another, and France against Spain. Meanwhile Denmark and Sweden fought for control of the countries surrounding the Baltic, and in Britain there was a civil war between royalists and parliamentarians.

his honesty and Johann Kunckel, who came earlier on the same mission, often mocked him, calling into question his right to call himself *Herr Doktor* Brandt. Kunckel was particularly bitter because of the way that Brandt had tricked him, yet he was to have the satisfaction of independently discovering how to make phosphorus and it was Kunckel who was often cited as *the* discoverer in the next century. Brandt revealed the existence of phosphorus in 1675, but in the years to follow it was other alchemists who basked in the fame of its awesome glow.

1675

Kunckel was born in 1630, the son of the court alchemist of Duke Frederick of Holstein. Like his father, he was attracted to alchemy and as a young man he obtained a position as alchemist to Duke Franz Carl of Sachsen-Lauenburg. In 1667, he moved to the Court of John George II, Elector of Saxony, but his post there was terminated in 1675 when it became clear that he was unable to turn lead into gold. Such was the esteem in which he was held, however, that he was offered a post teaching 'chemistry'* at the University of Wittenberg and it was there, in his laboratory, that Kunckel started investigating materials that shone in the dark.

At the time, a few materials were known that were luminescent, such as rotting wood and decaying fish, crystals of fluorspar (calcium fluoride) and Bologna stone (made from naturally occurring barium sulphate). This last mineral was first reported around 1640 by Vincenzio Casciorolo, an alchemist of Bologna. If crystals of Bologna stone were left in the sun during the day, they would glow for several hours during the night. The English

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* Chemistry then was more akin to alchemy, and is not recognizable as the science that it was to become in the following century.

diarist John Evelyn saw some on his travels in Italy in May 1645 and marvelled at their blue radiance.

Kunckel's interest in luminescence was heightened when he learned from a visitor that Hamburg was abuzz with talk of a new material that far outshone any other, including Bologna stone. Not only did this material glow in the dark for hour after hour, day after day, it did not need to be exposed to the sun in order to do so. Kunckel decided to seek it out, and he had not been long in that city before he learned of the man who possessed it: *Herr Doktor* Brandt. He called on Brandt, who was clearly flattered by his academic visitor and agreed to show him his phosphorus, although, as always, he was reticent about how he had made it. During the visit one of Brandt's children fell and grazed his face and, suspecting Brandt's title of *Doktor* was not genuine, Kunckel advised him to apply *oleum cerae* (oil of wax) to the child's cuts, whereupon Brandt revealed his ignorance by not recognizing this common medicament by its Latin name.

Even if he was not a medical man, Brandt was certainly an accomplished alchemist and there was no doubting that he had discovered a phosphorus to outshine all others. Kunckel was fascinated by what he saw and may even have offered to buy some of it to take back to Wittenberg to study. Brandt could well have entertained this idea because we know that he was again short of money, having spent most of his second wife's assets on his alchemical experiments. However, he was not prepared to sell the recipe for making it, which is what Kunckel really wanted.

Excited by what he had seen, Kunckel immediately wrote to a fellow alchemist, fifty-year-old Daniel Kraft, who lived in Dresden, describing the remarkable new phosphorus. Kraft immediately, and without telling Kunckel, rushed to Hamburg to see it for himself. He realized that this was a wonder indeed and, though he was sceptical about it being the philosopher's stone, he saw that it might well make gold in the right hands – his. He asked Brandt if he was willing to sell him some of his phosphorus. Indeed he was. In fact he would sell Kraft all that he had – and all that he could make in the future. Brandt could hardly believe his good fortune.

As Brandt and Kraft were talking there came a knock at the door, and when Brandt answered it he found Kunckel standing there. Quickly he stepped outside and closed the door behind him, saying that his wife was sick and someone was with her. Kunckel expressed a desire to know more about phosphorus and wanted to purchase some, but Brandt was suddenly reluctant to sell him any, saying he had none to spare and claiming that when he had recently tried to make more phosphorus he had had no success. When Kunckel again pressed him to say how it could be produced, Brandt, desperate to get rid of his unwanted visitor, admitted that it came from urine, but that was all he would say. He bade Kunckel farewell and went back indoors.

There Brandt continued his negotiations with Kraft and signed a bond for a fee of 200 thalers (about £4,000 or $6,000 in today's money), which gives us some indication of the dire financial straits in which Brandt now found himself. A few years earlier he and his wife had enjoyed an income of 1,000 thalers per year. Now he gave Kraft all the phosphorus he had and said he would make him more as required. Part of the deal was that Brandt should not talk about phosphorus to anyone and Kraft stressed that in particular he must never tell Kunckel how it was made. Brandt agreed.

The following day, Kunckel was surprised to meet Kraft in the street and asked why he had come to Hamburg. Kraft admitted that he had been to see the new phosphorus but said that he too had found Brandt difficult to deal with and that he could get nothing out of him about how it was made. On that note they parted and Kunckel returned to Wittenberg, where he began to experiment with urine. After several unsuccessful attempts to convert it to phosphorus he wrote to Brandt asking again how to make it, but Brandt's letter in reply said nothing, although he did reveal that he was now under an obligation to Kraft not to reveal the secret to anyone. Kunckel realized he had been tricked. He became all the more determined to discover how to make it himself and he soon succeeded.

1676

In the spring of 1676 Kraft put into operation his plan to make himself rich from his exclusive possession of the new phosphorus. He devised a series of dramatic demonstrations that he could perform with it and set out to travel the courts of Europe, where, for a fee, he would entertain royalty and courtiers with its remarkable properties. Like Brandt and Kunckel, Kraft was also an alchemist, although as a student he had graduated as an MD and, for a time, was employed as a physician by a mining company.

For the next two years Kraft displayed his phosphorus to most of the crowned heads of Europe. He even boasted to those who attended his demonstrations that he was the discoverer, and we know of this from the writings of one, Johann Elsholtz, who was invited to the display put on for the Elector of Brandenburg on the evening of 24 April 1676. At nine o'clock all the candles were extinguished and Kraft gave a demonstration of 'perpetual fire' for the benefit of the Court. Elsholtz came away from the event believing that Kraft was the discoverer of phosphorus and wrote as much when he published an account of what he had witnessed in a philosophical journal.

The French chemist and apothecary Nicholas Leméry also saw a demonstration by Kraft, probably at Paris, and he too said in his textbook of 1683, *Cours de Chymie*, that Kraft was the discoverer. Leméry had been particularly flattered when Kraft gave him a little of the new material and he even managed to cause an accident with it:

> After some experiments 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 bedclothes she had put upon the table, not seeing the little piece. The person who lay afterwards in the bed, waking at night and feeling more than ordinary heat, perceived that the coverlet was on fire.

Despite many failures, Kunckel had persisted with his experiments with urine and, in April 1676, he finally succeeded in producing a sample, a yellow blob in a sticky black mass. It hardly compared with Brandt's phosphorus, but Kunckel now felt confident enough to write again to Brandt suggesting they compare notes about their respective methods. Suspecting that this was merely a ruse to get him to reveal his recipe, Brandt replied that he was reluctant to send details via the post in case others should discover the secret. Kunckel suggested that he write in alchemical code, but no reply was forthcoming from Hamburg before 25 July, when Kunckel made a much better specimen of phosphorus. From that point on he realized he had no further need of Brandt. Brandt finally wrote, offering to sell the secret of his method, but Kunckel simply spurned the offer. Kunckel also made gold from his phosphorus by selling it as raw material for medicines, as we shall see in Chapter 3, and he too was invited to the courts of Saxony and Brandenburg to display his discovery.

Eventually Kunckel published a paper on the properties of phosphorus – although even he did not reveal how it could be made. By now he had become fascinated by its source, reasoning that what came out of the human body must also go into it. He investigated various foods and was amazed to discover that many things of plant or animal origin, when strongly heated in a furnace, were capable of producing phosphorus. He boasted that he could obtain phosphorus from all that God had created:

mammals, fish, birds, plants and trees. It was a remarkable observation, but he was right.

Kunckel's interest in phosphorus waned as his career developed. He was even quoted as saying: 'I am not making it [phosphorus] any more, for much harm can come of it.' In 1679 he became Director of the Alchemical Laboratory of Frederick William, Duke of Brandenburg, in Berlin and ten years later had risen to become Minister of Mines for all of Sweden, under Charles XI, where he was eventually honoured with the title Baron von Löwenstern. Kunckel died in 1703 but his fame as a chemist and his links with phosphorus were to endure. More than a century later, in his *Dictionary of Practical and Theoretic Chemistry*, published in 1808, William Nicholson referred to the element as Kunckel's phosphorus, calling it, so he thought, after its discoverer. By then Brandt's eclipse was total. What kept his name alive, and eventually regained him the title of the first person to make phosphorus, was the interest of Gottfried Wilhelm Leibnitz.*

1677

Kraft continued making his progress among the royal palaces of Europe, enjoying the fame and glory that his phosphorus brought. He never revealed the source of the new material and never mentioned Brandt. And so things might have continued had Kraft not gone to Hanover in 1677, there to perform before Duke Johann Frederick of Saxony. In his audience was thirty-

* Leibnitz is today remembered as the inventor of infinitesimal calculus, which transformed mathematics, but he was conversant with all branches of contemporary science including optics, mechanics, statistics, logic and probability theory. When he died at Hanover in 1716 most of his work was still unpublished.

one-year-old Leibnitz, who was employed as historian and librarian to the Duke. He was intrigued by the samples of phosphorus he saw and wanted to know more about it. How was it made? Kraft, of course, would not say.

A few months later, Leibnitz made a trip to Hamburg to buy books and there he learned, quite by chance, that a local man, Brandt, was also able to make the new phosphorus. Leibnitz searched him out and confirmed that this was so. Brandt, who by now was short of money again, was more than willing to explain that he, not Kraft, was the discoverer and that Kraft was merely exploiting him. In fact Brandt was by now refusing to supply Kraft with any more phosphorus, saying that all his attempts to produce it were proving unsuccessful. Leibnitz asked Brandt how he made phosphorus and Brandt not only freely admitted he got it from urine, he even offered to show his visitor how to make it – for a fee, of course. Leibnitz replied that he would enquire of Duke Frederick whether Brandt could come to Hanover to do this, and on that hopeful note they parted.

Brandt really was in need of money. Although he found reasons not to supply Kraft with any more phosphorus, it hardly mattered to Kraft who now knew that Kunckel had found a way to make it. In the spring of 1677, Kunckel had written to him offering to supply him with it but Kraft replied that he preferred Brandt's phosphorus as it was of better quality. Not that Kraft needed any more phosphorus, having almost exhausted the list of clients willing to view it. However, there remained one royal court Kraft had not yet visited where he knew he would be made most welcome and that was the Court of St James's in London. What transpired on that memorable visit we shall see in the next chapter.

After his visit to Hamburg, Leibnitz had returned to Hanover, where he suggested to the Duke that Brandt might be employed by the Court as the resident alchemist. The Duke agreed, saying he could be employed – at 10 thalers per month – and he accepted Leibnitz's suggestion that Brandt should receive six months' pay in advance if he revealed how phosphorus was made. On 18 July 1677, a contract was drawn up and sent to Brandt, which presented him with a rather awkward problem. Rebuffed by Kraft, Brandt let it be known that he was available for employment as an alchemist and one who already knew how to make the phosphorus. He had even entered into negotiations with a view to becoming resident alchemist for the Duke of Mecklenburg-Güstrow. He wrote to Leibnitz telling him of this, hinting that he was about to accept the post although nothing definite had been agreed.

Leibnitz persuaded Brandt to visit Hanover before deciding which offer to accept. On his return to Hamburg, Brandt made a final plea to Kraft, reminding him of their agreement and asking for more money, but Kraft was no longer interested and advised him to take the post at Hanover. Brandt's wife Margaretha wrote to Leibnitz on her husband's behalf asking for a higher salary, but to no effect. In the end, Brandt accepted the offer from Hanover, telling Leibnitz that he would need access to a small furnace and copious quantities of urine.

1678

Eventually, in the summer of 1678, Brandt journeyed to Hanover, and there outside the city he set up his apparatus, and with Leibnitz's help he made some phosphorus. Leibnitz was duly impressed with its quality and properties which were exactly those he had witnessed when Kraft had put on his demonstrations for the Duke. When he asked Brandt how he had discovered phosphorus, Brandt told him that he had first made it in 1669, and said that he got the idea from a book by F. T. Kessler of Strasbourg called *400 Auserlesene Chemische Process* ('400 Selected Chemical Processes'), published in 1630, in which there was a recipe for turning base metals into silver using concentrated urine, alum and saltpetre.*

Brandt returned to Hamburg, promising to make more phosphorus there and send it to Leibnitz, but nothing was forthcoming. Leibnitz wrote to Brandt a few times, querying his silence, until on 11 December 1678 he finally received a reply from the alchemist who claimed that he had been unable to work because he and two of his children had been ill and that his eldest daughter had died. Brandt asked Leibnitz for more money, and after a further exchange of letters and an increased allowance of 10 thalers per week he agreed to return to Hanover and make more phosphorus. Again the experiment was a success, so much so that Leibnitz now published an account of how to make phosphorus from urine, although he omitted to mention the debt he owed to Brandt. It was not that Leibnitz wanted to deny the tiresome alchemist his rightful claim to be the discoverer: whenever he was asked about it he would admit that Brandt had shown him how to make it.

Perhaps not surprisingly, since Brandt's name was missing from all the early accounts of phosphorus, his contribution was overlooked by succeeding generations of scientists, and he was soon forgotten. About what happened to Brandt after his second trip to Hanover we know virtually nothing. He lived to be at least sixty because he was still alive in 1692, according to Leibnitz, and even in 1710 Leibnitz said that he had not heard of his death, which could mean that he lived to be eighty or more. If so, Brandt must have been aware that by then his discovery had fostered a new industry in London, and a vogue for taking the element as a medicine. What rescued Brandt from oblivion was Leibnitz's papers, among which were the letters from Margaretha.

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* Alum is potassium aluminium sulphate, and saltpetre is potassium nitrate. Needless to say the recipe rarely, if ever, succeeded.

Phosphorus – the unanswerable questions

Whatever Brandt's fate, his place in the story of chemistry was assured by his fame, or notoriety, in being the first person to have discovered phosphorus. The shocking history of phosphorus had begun. From our vantage point of the twenty-first century we can answer the questions these early investigators must have asked themselves: What is phosphorus? Why does it glow in the dark? How can it be produced from urine?

The first is easy to answer: phosphorus is a chemical element. Its properties are now well known, its forms varied and its chemistry well understood – see Appendix below, p. 303.

The second question proved unanswerable for more than 300 years. The famous painting *The Alchymist* by Joseph Wright of Derby (1734–97) – Plate 1 – captures the wonder of the discovery but exaggerates the intensity of the light that it emits. Even so, the glow from phosphorus is impressive and, although other ways of generating light by chemical reactions are now known (see box), the length of time that phosphorus will glow is still remarkable.

It was not until 1974 that the correct explanation for phosphorus's luminescence was forthcoming. It was revealed by R. J. van Zee and A. U. Khan in the *Journal of the American Chemical Society* (p. 6805). The explanation lies in the slow chemical reaction between phosphorus and the oxygen of the air which takes place on the surface of phosphorus, forming two species which have only a fleeting existence: a molecule of formula HPO and an oxide of formula P_2O_2. Both emit visible light. Very little of these unstable species need be formed to produce the luminescence, which is why a piece of phosphorus in a closed vessel continues to glow for hours and days, until the last trace of oxygen has been used up.

How can phosphorus be produced from urine? This waste

Living things that give off light

Although the words phosphorus and phosphorescence derive from the same Greek word, phosphorus's glow is not due to phosphorescence. Phosphorescence is the process whereby light is first absorbed by a body and then re-emitted from it some time later; Bologna stone is phosphorescent.

Phosphorus itself is *luminescent*. Luminescence describes the process in which light is emitted as a result of an energy change within a substance, and there are many living things that can luminesce, such as flies, fungi, fish and jellyfish. (The technical term for this is *bio*luminescence.) Even some bacteria are able to emit light, which accounts for the luminescence that occurs in the wake of a boat at sea, or the glow of decaying wood and fish. All produce a chemical, luciferin, which is a sulphur–nitrogen compound, and an enzyme, luciferase, which enables the luciferin to react with oxygen and as it does so it releases some of its energy in the form of visible light. The genes responsible for bioluminescence have been identified in the light-emitting bacterium *Photorhabdus luminescens*, and research is now going on into transferring these into other organisms to act as biological sensors.

material remained the only source of the element for nigh on a century, and it is easy to understand why: phosphate is one of the most abundant components of urine because human beings take in much more phosphate from their diet than they actually need. Most of the excess phosphorus is passed in the urine as phosphate, at the rate of around 1.4 g phosphorus per day.* The main chemicals in urine are given in Table 1.1.

* The body also loses phosphorus through the faeces, but less is excreted

Table 1.1: The chief components in urine (grams per litre)

Constituent	*Adult male*	*Adult female*
Creatine	52	92
Urea	21	21
Chloride	6.5	4.7
Sodium	4.0	2.9
Potassium	2.2	1.8
Amino acids*	*ca* 2.3	*ca* 2.3
Phosphorus	1.4	1.4
Ammonia	0.68	0.51
Magnesium	0.26	0.21

* Chiefly glycine, histidine and taurine.
Data adapted from K. Diem and C. Lentner, eds, *Scientific Tables*, 7th edn, J. R. Geigy, Basle, 1970.

To release phosphorus from phosphate requires carbon, which in turn requires some form of organic matter to be decomposed by intense heat. Urine contains several organic chemicals that can act as a source of carbon, such as creatine, which is a constituent of all cells but especially of muscle fibre. Another abundant organic component is urea, but there are also others such as amino acids, various carbohydrates and enzymes.

Urine not only fascinated the alchemists but it also had important commercial uses in dyeing, scouring and the making of simple chemicals such as sal ammoniac (ammonium chloride) and saltpetre (potassium nitrate). The processing of urine had

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in that way. The average adult passes around 120 g (4 ounces) of solid waste matter each morning, 75 per cent of which is water and 0.8 g of which is phosphorus. The total daily loss of phosphorus by the average adult is therefore 2.2 g.

started in the days of the Roman Empire, when vast quantities were collected for industrial use.

In *The Chemical Works of Caspar Neumann MD*, published in 1759 by the eponymous professor of chemistry at Berlin, there is a description of the components that could be separated from urine by distillation: spirit of urine, oil of urine and phosphorus of urine. The oil was even rumoured to taste as sweet as sugar. It was also possible, by slow evaporation, to grow crystals from urine which were known as microcosmic salt (sodium ammonium hydrogen phosphate, formula $Na(NH_4)HPO_4.4H_2O$). These play a part in the phosphorus story, as we shall see in Chapter 10.

According to Neumann, 60 gallons of urine could be evaporated to yield 10 pounds of dry matter which, on further heating, lost a third of its weight and from which eventually an ounce, or more, of phosphorus could be obtained. We learn from his book that, to get phosphorus, you needed a furnace of the type used by glass-makers. He also says that phosphorus could be purified by heating it in boiling water, stirring until the liquid phosphorus becomes clear. Phosphorus produced in this way was given a variety of names: *phosphorus urens*, *phosphorus glacialis* or *noctiluca glacialis*.

The volume of urine necessary to produce phosphorus using Brandt's method was truly enormous because his process was so inefficient. We know that Brandt told Leibnitz it would require 5 tuns of urine to produce a mere 2 loths of phosphorus.* The process was made unnecessarily complicated, as we can see from the first recipe published in English for making phosphorus. This is given in *Philosophical Experiments and Observations of the Late Eminent Dr Robert Hooke FRS*, which was written by a Dr Derham and published in 1726. It began as follows:

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* A tun was a large wine cask capable of holding around 1,100 litres, while a loth was about 60 grams.

> 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, or else it may be doing a fortnight or more . . .

The account went on to describe how it was necessary to heat the residue in a retort for up to twenty-four hours in order to produce phosphorus. Derham also warned of its dangers:

> Mr Concle [Kunckel] writ also with it on paper and the letters all shined in the dark . . . He once wrapped up a knob of it in wax at Hanover and it being in his pocket and he busy near the fire, the very heat did set it aflame and burned all his clothes 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.

Brandt's method of making phosphorus, as described by Leibnitz, required several stages. The thick syrup that urine was reduced to was heated until a red oil distilled over and this was collected. The retort was allowed to cool and its contents consisted of a black and spongy residue in the upper part and a lower part that was salty. This salt was discarded. The black material was scraped off and mixed with the red oil, and the two were put back into the retort and heated for sixteen hours, during which time white fumes came off first, then another oil and then phosphorus, which was passed into cold water to solidify.

Brandt got only a little phosphorus because he did several things wrong. To begin with there was no need to leave the urine to putrefy. This does nothing to increase the amount of phosphorus, nor does it aid extraction. As others discovered later, using

The alchemy of phosphorus

Phosphate consists of a central phosphorus atom surrounded by four oxygen atoms and carrying three units of negative charge, in the form of electrons, so it is written PO_4^{3-}. These negative charges have to be counterbalanced by three positive charges, which might take the form of sodium (Na^+), this being the most abundant metal element in urine. To release the phosphorus from the strong grip of the four oxygens requires four carbon atoms to prise them off, thereby forming the gas carbon monoxide (CO). If sand is present, this reacts with any metals present to form silicates such as sodium silicate, Na_2SiO_3.

To generate these chemical reactions a great deal of heat is necessary. The overall chemical change is:

sodium phosphate + carbon + sand + heat → phosphorus + carbon monoxide + sodium silicate

Even today this is still essentially the same process for making phosphorus, except that calcium phosphate ore is used, the carbon comes from coke and the heating takes place inside an electric furnace.

fresh urine gave equally good results. Strong heating of the urine residue causes all kinds of chemical reactions to occur, driving off volatile organic matter as an oil, but this contains almost no phosphorus because phosphates are not volatile.

The residues left in the retort after this first heating can be identified as a black char of carbon, formed by the decomposition of organic material, and the salt layer. By discarding this Brandt was throwing away most of the phosphate, which explains why the amount of phosphorus he got was so small (less than 1 per cent of what would have been present in the urine). Had he ground the contents of his retort together to get an intimate mix of the carbonized layer and the salt and then heated that, he might well have increased his yield of phosphorus from 50 g to 500 g or even 5,000 g.

The method eventually published by Kunckel was similar except that he mixed the urine paste with fine sand before heating it in a retort. The use of sand gave an increased yield because it combines with the salts present, thereby aiding the decomposition of the phosphate.

Since all that is required to make phosphorus is urine and heat, it is reasonable to wonder whether phosphorus was, in fact, discovered prior to the seventeenth century. There are intriguing references throughout history to curious materials that might just have been phosphorus. For example, it might even have been known in Roman times. St Augustine, the Christian theologian and philosopher who lived from AD 354 to 430, wrote of 'perpetual' lights that were seen in the sepulchres of the early Christians. This is unlikely to have been a reference to phosphorus the element, but he might have been referring to another form of phosphorus, as we shall discover in Chapter 14.

The fourteenth-century French alchemist Achid Bechil referred to a curious 'carbuncle' that formed when he distilled urine mixed with clay, lime and other organic matter. Such a mixture might indeed give off phosphorus if heated strongly enough and this could explain Bechil's observations. But, because he does not refer to the carbuncle either glowing in the dark or bursting into flames, it seems unlikely that he had really made phosphorus.

More reliable was a report by the Swiss-born alchemist and physician Paracelsus.* He is best known as the founder of

* His real name was Theophrastus Bombastus von Hohenheim and he lived from 1493 to 1541.

modern medicine, and published a recipe in his *Archidoxorum* for the distillation of urine. In this report he says that water, air and earth will ascend together and the fire remains behind. All are recombined and distilled a second, third and fourth time, at which point the earth will remain behind. Cooling the material that distils produces 'icicles, which are the elements of fire'. This sounds tantalizingly like a reference to phosphorus. Yet, if Paracelsus really had discovered the real thing, he would surely have made more of his discovery and we are forced to conclude that his icicles were not phosphorus. In fact there is no convincing evidence to suggest there was an earlier discovery of phosphorus prior to the experiments of Brandt.

△

That phosphorus was an element was not appreciated at the time of its discovery. Another century was to pass before the French chemist Antoine Lavoisier first postulated that all matter is composed of *chemical* elements, and listed many of them, including phosphorus. Today we can place the discovery of phosphorus in the historical context of the discovery of the elements. It was the thirteenth chemical element to be isolated in its pure form.* Unlucky phosphorus.

To begin with, phosphorus was greeted with great acclaim, and yet it was damned from the moment it was born. It displayed properties that humans were in no position to cope with. As we shall read in Chapter 3, phosphorus promised cures but it delivered mainly curses. It is a deadly poison and yet soon after its discovery it was being sold by pharmacists as a treatment for all kinds of illnesses and especially mental conditions. Even more

* The others, in the order in which they were discovered, were: carbon, sulphur, copper, silver, gold, iron, tin, antimony, mercury, lead, arsenic and bismuth. These twelve occur naturally, or were easy to win from their ores, or were discovered by individuals unknown.

remarkable, it was to remain part of the medical pharmacopoeia well into the twentieth century, despite its having cured no one of anything in the previous 250 years.

While doctors used phosphorus, hoping to cure their patients, others used it to murder them (Chapter 9); and while some scientists were researching it with a view to making pesticides to benefit human beings, others were secretly turning it into nerve gases, the better to destroy them (Chapter 8).

Even Nature finds it difficult to control phosphorus, having assigned to it the role of limiting all life on Earth (Chapter 12). Phosphorus is in short supply, yet is essential for every living cell. However, when humans increase the amount in the environment by using it as fertilizers and detergents, the life-forms that flourish may not be the ones we want (Chapter 13).

Phosphorus has the power to burst into flames; again a mixed blessing. Its ability to burn was put to use in various ways down the ages, starting with phosphorus tapers and phosphorus matches (Chapter 4), and ending with phosphorus bullets and phosphorus bombs. The irony was that Hamburg was to be devastated by phosphorus in the twentieth century, when tens of thousands of its citizens would be burned alive by it (Chapter 7). Back in seventeenth-century Hamburg all this was well into the future, but, for good or evil, the genie of phosphorus had been loosed on the world.

Phosphorus was discovered when the practice of alchemy was giving way to chemistry. If a single chemical can be said to have precipitated that change, it was phosphorus. If a single event in the history of this element was responsible, it was Kraft's final demonstration of its remarkable properties at a private house in London one September evening in 1677, as we shall see in the next chapter.