Phosphorus

From Elemental Light to Chemical Element

By F. Krafft[*]

Exactly 300 years ago in the city of Hamburg, a certain Hennig Brand, self-styled doctor medicinae, and chymist, discovered a strange substance in human urine, which was later called phosphorus (light bearer), a name then common to various luminous substances, and which created much excitement in the latter years of the 17th century on account of its properties. However, it was not Brand who profited from the discovery but others: Johann Daniel Krafft, Johann Kunckel, and Gottfried Wilhelm Leibniz, men who knew only too well how to exploit the weaknesses of the discoverer. "Cold fire", Brand's own name for the new substance, was originally regarded as elemental light or fire, and it was not until the conception of the antiphlogistic theory by Antoine Laurent Lavoisier that the proper position of phosphorus among the chemical elements was recognized. In fact, the element played a decisive role in the overthrow of the phlogiston doctrine, a little over one hundred years after its discovery and almost two hundred years ago.

1. The Year of the Discovery

In his paper 'Historia inventionis phosphori' [1], which was published in 1710, *Gottfried Wilhelm Leibniz* writes: "Inter inventa nostri saeculi non minimum habendum est phosphorus igneus . . ." "Not least amongst the discoveries of our time is phosphorus igneus, which differs from other substances in that it is nothing other than a hidden fire (ignis quidam tectus) that manifests itself in light and smoke and bursts into flames when rubbed. This discovery became public knowledge around the year 1677 (Id inventum circa annum 1677 prodiit . . .). . ."

Johann Daniel Krafft (Kraft, Crafft; 1624–1697), however, Councillor of Commerce to the Saxon elector at Dresden, had already demonstrated the substance, together with three other kinds of "phosphorus," at the court of the Grand Elector *Friedrich Wilhelm von Brandenburg* at Berlin on April 24, 1676, but without making any reference to the discoverer or to the origin of the substance. The demonstration is recorded by the Court Physician *Johann Sigismund Elsholz* (1623–1688) in a document entitled 'De phosphoris quatuor observatio' and dated May 20, 1676 [46]. In September 1677 the same *Krafft* informed *Robert Boyle* (1627–1691) that one of the samples of phosphorus he had received from *Brand* had continued to luminesce for two years [2].

At the same time, *Johann Kunckel* (1630–1703), one of the most highly esteemed "chymists" of the day, was also in possession of this substance. A friend of his, *Georg Caspar Kirchmaier* (1637–1700), Professor of Rhetoric at Wittenberg, gives an account in his short treatise 'Noctiluca constans et per vices fulgurans, diutissime quaesita, nunc reperta', the foreword to which is dated September 11, 1676 (Chapter 3: De noctiluca aliqua constanti):

"Almost six months have passed since he (*i.e. Kunckel*) first revealed to me that he possesses the 'eternal light' . . . I will not say how long this skilled man spent in collecting and preparing the starting material, but will be content to have mentioned that when he repeated the work – not before July 25 – he obtained but little more than half an ounce, in spite of the fierce fire which was kept burning for many hours."

Kunckel himself reports later in his 'Collegium physico-chymicum experimentale' [3], which was published posthumously, that he learned of *Brand*'s phosphorus while staying at Hamburg just a few weeks after the discovery of *Balduin*'s phosphorus. He states, incorrectly, that the latter, a calcined calcium nitrate, was discovered in the year 1677. In fact, the Saxon magistrate *Christoph Adolph Balduin* (1632–1682) had already reported on his discovery in 1674 in 'Miscellanea curiosa medico-physica Academiae naturae curiosarum sive Ephemerides medico-physicae Germaniae' [4] and written a special treatise in the following year [5]; in neither case, however, does he disclose the method of preparation.

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[1] *G. W. Leibniz*: Historia inventionis Phosphori. Miscellanea Berolnensia ad incrementum scientiarum *1*, 91–98 (Sumptibus J. Ch. Papenii, Berlin 1710).

[2] *R. Boyle*: A Short Memorial of some Observations made upon an Artificial Substance, that shines without any precedent Illustration (Sept. 1677). Lectures and Collections made by Robert Hooke, Secretary of the Royal Society, London 1678, p. 57–66 (reprinted in *R. T. Gunther*: Early science in Oxford, Vol. VIII. Oxford University Press, Oxford 1931, p. 273–282).

[3] *J. Kunckel*: Collegium physico-chymicum experimentale oder Laboratorium Chymicum. Hamburg-Leipzig 1716 (²1722), p. 660–665.

[4] *Ch. A. Balduin* in: Miscellanea curiosa medico-physica Academiae naturae curiosarum sive Ephemerides medico-physicae Germaniae. Annus quartus et quintus 1673/74, p. 121.

[5] *Ch. A. Balduin*: Aurum superius et inferius aurae superioris et inferioris hermeticum et phosphorus hermeticus sive magnes luminaris. Frankfurt-Leipzig 1675.

Thus the seventeenth-century printed sources cited here suggest early 1676 as the date of the discovery of phosphorus igneus, as it was called by *Leibniz*. Even in 1784, *Lorenz Crell* referred to these data in a note accompanying his paraphrased translation of *Leibniz*' 'Historia'[6]. He had, however, understood the year 1677 given by *Leibniz* to be the year of the discovery, for he paraphrases the passage quoted above as: "Phosphorus, that remarkable invention of our century, was discovered in 1677." (The same conclusion is reached by *J. S. T. Gehler*[7], *J. C. Fischer*[8], and others.) On the basis of the sources cited, *J. R. Spielmann* had previously, in 1766, decided in favor of the year 1674 or 1675 for *Brand*'s discovery[9], followed shortly by *J. C. Wiegleb*[10].

Thus it is hardly surprising that to our time these years are continually given as the supposed date of the discovery of phosphorus: *E. Färber (Farber)*[11,12], *J. R. Partington*[13]; *A. Wolf*[14] on the other hand writes: "the dates given vary from 1667 to 1674", and simply takes an average: "sometimes about 1670" (with which *P. Walden*[15] also concurs). Even the authors of the historical section of the latest (1965) edition of 'Gmelins Handbuch der anorganischen Chemie'[16] still shared the opinion of *Spielmann* and *Wiegleb* stating: "that ... the years 1674 and 1675 come into question as the date of the discovery of phosphorus."

However, "it is in the interest of science that the history of memorable discoveries (historia inventionum memorabilium) be handed down accurately", as *Leibniz* states in the opening passage of his 'Historia'. In this treatise *Leibniz* himself actually sets the date of the discovery as 1669, provided that one correctly interprets the information that he gives. Unlike *Kunckel*, who lost no opportunity to play down, in a rather ungentlemanly fashion, the credit due to *Brand* in favor of his own claims to the discovery, or at least to the independent rediscovery of phosphorus, and on whose information, both written and oral, all other contemporary versions of the history of the discovery are directly or indirectly based, *Leibniz* takes great pains to provide an objective report, in spite of later differences with *Brand*. He was well acquainted with the Hamburg chymist, recognized also by *Krafft* and *Kunckel* as the first discoverer, or at least better acquainted than those who had met him during a single visit to Hamburg, for he corresponded with him over a considerable period of time, visited him in Hamburg, and on two occasions was able to persuade him to visit Hanover for a relatively long time to prepare phosphorus. Moreover, *Leibniz* himself made no claim to the discovery.

On April 30, 1962, *Wilhelm Homberg* (1652–1715) presented a report to the Paris Academy dealing with the discovery and the purported rediscovery of phosphorus by *Kunckel*. In *Leibniz*' opinion, this paper contains several grave errors which he immediately critized, apparently in vain for no correction ever appeared. Thus, "Itaque ne veritas rei gestae, non multis fortasse hodie nota, intercedat" he published his 'Historia inventionis Phosphori'. Before proceeding to correct the various errors he presents a Latin version of Homberg's report[17]:

"Prima inventio huius Phosphori casui debetur, ut multa alia pulchra inventa. Chymista quidam Germanus, cui nomen *Brand*, Hamburgi degens, homo obscurus, humilis originis, ingenio moroso et phantastico, et in omnibus, quae agebat, mysteriosus, materiam hanc luminosam aliud quaerens invenit. Vitrariae artis deditus erat a iuventute, sed hanc deseruerat, ut lapidi philosophico vacaret, cuius spes animum eius invaserat. Cum ergo sibi persuasisset, secretum Lapidis in praeparatione urinae consistere, diu et multipliciter in ea laboravit frustra: tandem anno 1669 post fortem urinae destillationem in recipiente invenit materiam lucidam, quae postea Phosphori nomen obtinuit. Hanc monstravit amicis quibusdam, et inter alios *Kunkelio* Chymistae Electoris Saxoniae, sed cavit, ne quid diceret, inde compositio cognosci posset, obiitque secreto suo nemini communicato. Post obitum eius *Kunkelius* tam pulchrum arcanum perire non aequo animo ferens, resuscitationem inventi aggressus est, et considerans *Brandium* tota vita in urina laborasse, suspicatus est, in ea Phosphorum esse quaerendum. Huic ergo operam dedit, et post pertinacem quadriennii laborem, tandem, quod quaerebat, invenit. Non aeque mysteriosus fuit ac *Brandius*, arcanum ne nonnullis communicavit circa annum 1679. In Gallia et Anglia *Kraftius* Medicus Dresdensium, inventor huius Phosphori habetur, quoniam eum primus illuc attulit. Sed revera non nisi dispensator eius fuit, quem a *Kunkelio* acceperat, ut eruditis exteris ostenderet. Immo ignorabat compositionem *Kraftius* tunc, cum itinera sua obiret."[*]

[6] *L. Crell*: Lorenz Crells Neues Chemisches Archiv, Vol. 1, 2. 213 (1784).

[7] *J. S. T. Gehler*: Physikalisches Wörterbuch oder Versuch einer Erklärung der vornehmsten Begriffe und Kunstwörter der Naturlehre ... 3. Theil. Schwickertscher Verlag, Leipzig 1790, p. 481.

[8] *J. C. Fischer*: Physikalisches Wörterbuch oder Erklärung der vornehmsten zur Physik gehörigen Begriffe und Kunstwörter ... Dritter Theil. J. Chr. Dieterich, Göttingen 1800, p. 872.

[9] *J. R. Spielmann*: Institutiones Chemiae. 2nd Edit., Strasbourg 1766, p. 223.

[10] *J. Chr. Wiegleb*: Geschichte des Wachstums und der Erfindungen in der Chemie, in der neuern Zeit. Ersten Bandes erster Theil, von 1651 bis 1700. F. Nicolai, Berlin and Stettin 1790, p. 39–42.

[11] *E. Färber*: Die geschichtliche Entwicklung der Chemie. J. Springer, Berlin 1921, p. 56.

[12] *E. Farber*: The evolution of chemistry. A history of its ideas. methods, and materials. Ronald Press Co., New York 1952, p. 83,

[13] *J. R. Partington*: A short history of chemistry. 3rd. Edit. MacMillan, London 1957, p. 62.

[14] *A. Wolf*: A history of science, technology and philosophy in the 16th and 17th centuries, Vol. 1. 2nd. Edit. MacMillan, New York 1959, p. 348.

[15] *P. Walden*: Chronologische Übersichtstabelle zur Geschichte der Chemie von den ältesten Zeiten bis zur Gegenwart. J. Springer, Berlin 1952, p. 17.

[16] Gmelins Handbuch der Anorganischen Chemie. 8th Edit. System-Nummer 16: Phosphor; Teil A. Verlag Chemie, Weinheim/Bergstr. 1965, p. 8.

[17] Cf. ref. [1], p. 92.

[*] "Like so many other beautiful discoveries (inventa), the discovery of this phosphorus was due to a coincidence. A German chemist named *Brand* who lived at Hamburg, an unknown man of humble origin, of a morose and fanciful nature, and secretive in all that he did, discovered the luminous substance while searching for something else. From his youth he had occupied himself with the art of glassmaking but had forsaken this art in order to devote time to the philosopher's stone, upon which he had set his hopes. When he reached the conclusion, that the secret of the stone consisted in the treatment of urine, he frequently spent long periods working vainly with the latter. At length, in the year 1669, after vigorous distillation of the urine, he found a luminous material in the receiver which was later given the name phosphorus. This he showed to some friends and, among others,

If this report is compared with information given by *Kunckel* in his own works on the discovery of phosphorus and with that contained in letters to and from *Leibniz* and *Brand* – particularly in the correspondence between *Brand, Leibniz, Krafft*, and *Kunckel* of 1676 to 1679, which was first cited by *H. Peters* in 1902 [18] and then published in its entirety in 1916 [19] it becomes clear that *Homberg* must have heard the details from *Kunckel* himself. *Homberg* also states that he visited *Kunckel*, who had been appointed "Chymist" in the service of the Grand Elector in 1679, in Berlin, and received from him the procedure for the preparation of phosphorus [20]. Thus the mere fact that the name *Brand* and the year 1669 can be traced back to *Kunckel* imparts credibility to these statements. Moreover, *Leibniz*' detailed corrections – the death, the character, and the ability of *Brand*, and concerning *Brand*'s reports to *Krafft* and *Kunckel* – which follow the reprinted passage, make no further mention of the date. It must therefore agree with that which *Brand* had told him (*Kunckel* too can only have heard it from *Brand*), and the fact that *Brand* himself had told *Leibniz* of his discovery is clear from several details that are retold only by *Leibniz*, and particularly from the report that the motivation for his investigations on urine came from a printed work on alchemy: "Inciderat Brandius in processum quendam chymicum in libro typis edito, exantem, qui ex urina parare docebat liquorem aptum (si credimus) particulae argenti in aurum muturandae" [21].

Since phosphorus igneus remained unknown outside Hamburg until 1676, when *Krafft* and *Kunckel* were shown it by *Brand* and given samples, and since no earlier date is given in connection with or by *Krafft* – who only occasionally failed to mention the name of the discoverer but never claimed to be the same – or by *Kunckel*, there was no reason for *Brand* to subsequently pre-date his discovery. So long as no new contradictory sources become available there appears to be little reason for scepsis concerning *Brand*'s claim to have discovered the substance which he called "my fire" or "cold fire" in the year 1669, exactly three hundred years ago.

Kunckel, Chymist to the Saxon Elector, but took care to say nothing that could reveal the composition, and died without having told anyone his secret. After his death, *Kunckel*, who was not indifferent to the loss of such a beautiful secret, set about the resuscitation of the discovery; and considering that *Brand* had spent his whole life working with urine, he suspected that phosphorus was to be found in this substance. He therefore directed his attention to the latter, and, after four years' intense work, discovered that which he sought. He was not so secretive as *Brand* and he made the secret public around the year 1679. In France and in England, *Kraft*, a Dresden physician, is held to be the discoverer of phosphorus since it was he who first took it to those countries. In fact he was merely the distributor of the phosphorus that he had received from *Kunckel* to show to foreign scholars. *Kraft* was not even aware of the preparation when he undertook his journeys."

[18] *H. Peters*, Chemiker-Ztg. *26*, 1190 (1902).

[19] *H. Peters*, Arch. Gesch. Math., Naturwiss. Techn. *7*, 85 (1916).

[20] *W. Homberg*, Manière de faire le phosphore brulant de Kunckel. Mémoires de l'académie royale des sciences à Paris, depuis 1666, jusqu'à 1699 *10*, 57 (Paris 1730).

[21] Cf. ref. [1], p. 93.

The year 1677 (circa annum 1677) given by *Leibniz* does not refer to the discovery of phosphorus but to the disclosure of the discovery (prodiit!) – and outside Hamburg this actually took place in the year 1676/1677. *Leibniz* himself first became acquainted with phosphorus during a demonstration to the Hanoverian court by *Krafft* in mid-1677, and he immediately reported what he had seen in 'Journal des Savants' [22]. There he states: "...if the liquid is placed on any object outside the phial then the light disappears within a short time ..., but if it remains in the closed phial it is preserved for several years. *And it has actually been kept for two years*", *i.e. Leibniz*, too, recognized the discovery as being of an earlier date. (The year 1669 is also given in [7, 8, 23–32], but in no case does the author give any proof.)

2. The Discoverer

In the 17th and 18th centuries the substance known by *Leibniz* as "Phosphorus igneus", "Pyropus" (Greek: fiery-eyed), and "Phosphorus κατ' ἐξοχήν" [33] was given a whole variety of names, some of which referred to its properties, while others were intended to refer to the supposed discoverer. Thus *G. C. Kirchmaier* [34] calls it "*Kunckel*'s phosphorus", a name that rapidly found general acceptance and soon became the only name in common use, since in his publications *Kunckel* had claimed [35] as his own the discovery, or at least the rediscovery and the first planned preparation, while enjoying the support of his friend *Kirchmaier*, and later also that of *Homberg* (1692) [20], *J. H.*

[22] *G. W. Leibniz*: La phosphore de M. Krafft ou Liqueur et terre secche de sa composition qui jettent continuellement de grands éclats de lumiere. Le Journal des Scavans du Lundy 2. Aoust, 1677. Paris, p. 244.

[23] *J. S. T. Gehler*: Physikalisches Wörterbuch; neu bearbeitet von *Brandes, Gmelin, Horner, Muncke, Pfaff*, Vol. 7, 1. Abth. E. B. Schwickert, Leipzig 1833, p. 474 (*Gmelin*).

[24] *H. Kopp*: Geschichte der Chemie. 4 Bde. F. Vieweg & Sohn, Braunschweig 1843–1847. Vol. 2, p. 233; cf., however, Vol. 3, p. 327ff.

[25] Cf. ref. [18], p. 1191.

[26] Cf. ref. [19], p. 88.

[27] *W. Herz*: Grundzüge der Geschichte der Chemie. Richtlinien einer Entwicklungsgeschichte der allgemeinen Ansichten in der Chemie. F. Enke, Stuttgart 1916, p. 38.

[28] *E. v. Meyer*: Geschichte der Chemie von den ältesten Zeiten bis zur Gegenwart. 4th Edit. Veit u. Co., Leipzig 1914, p. 133.

[29] *H. Valentin*: Geschichte der Pharmazie und Chemie in Form von Zeittafeln. 3rd Edit. Wiss. Verlagsgesellschaft, Stuttgart 1946, p. 37.

[30] *E. Pilgrim*: Entdeckung der Elemente mit Biographien ihrer Entdecker. Mundus-Verlag, Stuttgart 1950, p. 78.

[31] *A. J. Ihde*: The development of modern chemistry. Harper and Row, New York 1966 (1964), p. 747.

[32] *E. Farber*, U.S. nat. Museum, Bull. *240*, 177 (1966) (not available to the present author).

[33] Cf. ref. [1], p. 92.

[34] *G. C. Kirchmaier*: Nocticula constans et per vices fulgurans, diutissime quaesita, nunc reperta. Wittenberg 1676, p. 12.

[35] *Kunckel*'s report [3] (Historia von dem Phosphoro, welchen einige Lumen constans genennet) is reprinted in parts in ref. [16], p. 13, as an English translation by *T. L. Davis*, J. chem. Educat. *4*, 1105–1110 (1927).

Cohausen[36], and *Hellot* (1737) – in spite of *Leibniz*' justified opposition – and most of the older versions of the discovery of phosphorus. *Leibniz* comments[37]:

"But it is all the more amazing that he [*i.e. Brand*] is reported dead at the time when *Krafft* and *Kunckel* were spreading the news of the discovery of phosphorus throughout the world by the spoken and written word, and that *Kunckel* should have reawakened the art that had been lost with the original discoverer, while it is beyond doubt that *Kunckel*, while visiting *Brand*, had been initiated in the art by the latter, and that *Brand* lived for a long time and complained about *Kunckel*... But when *Kunckel* had returned home and made not few mistakes in the manipulations (in enchiresi), he was for a long time unable to prepare the phosphorus and sent letters of complaint to *Brand*, which I have seen, and in which he lamented that he had not told him the secret sufficiently openly. However, *Brand*, who regretted that he had been so thoughtless as to divulge his secret, refused to show the erring *Kunckel* the way. In the meantime, *Kunckel* corrected his mistakes himself, whence arose the pretentiousness (praetensio praetextusque), to dare to pose as the discoverer wherever he went, about which *Brand* complained bitterly."

Fortunately, *Leibniz* did not return *Kunckel*'s letters to *Brand* to the latter so that the accuracy of *Leibniz*' information can be confirmed to this day, and likewise *Kunckel*'s untruthfulness when he claimed (1713)[3,35] to have given *Brand* no promise of secrecy. While still on the homeward journey *Kunckel* wrote the following lines to *Brand* from Magdeburg in March, 1676[38]:

"Salve! Insonders hochgeehrter Doctor, zuverlässiger, wehrter Freundt, ehr wird sich wohl entsinnen, was wir mit einander abgeredet, nehmlich dass ehr mihr das lumen in einem Glase wollte nachschicken, nu sehe der Herr zu, dass ehrs in ein fein Cristallglas kricht und sende es mit dem ersten, dass ichs seh, dan ich habe darauf was herrlichs ausgesonnen..." [*]

At Wittenberg he then attempted to prepare phosphorous according to the information given to him by *Brand*; apparently without success for on June 25, 1676 he wrote[39]:

"... Wie angenehm mir des Herrn Doctors Brieflein von 3. Juni gewesen, kann ich nicht genug schreiben. Sehe daraus dessen gute Zuneigung, ehr had dakegen sich zu versichern, wass ich ihm so theur zu geschworen, dass ichs ehrlich halten wil, lebe auch der Hoffnung, der Herr Doct. wirt mir sein Feur getreuhlig geben; die Entschuldigung, dass ehrs der Feder nicht zu trauen darf, davohr trage ehr keine Sorge; der Herr Doctor schreibe so, ehr nehme die bewusste Materie, so oder so vihl, setze dieses darzu und mache es so, wehr wil das verstehn... Ich bitte dem Herrn, ehr solle mihr als ein gutter Freunt trauen, gebe es keinen Menschen mehr und lass mihr sorgen; so verne ehr es mir communicirt, wil ich, so wahr ich wil teihl an Gottes Gnade haben, so mit ihm handeln, dass ehr und die Seinigen sollen mihr Dank wissen, aber ehr muss mihr ohn Massgebung folgen... Der bewussten Matterie habe ich ein ziemlich Teyl. Habe es 2 mahl destilliert, aber kein Feuer gekricht. Bitte der Herr lasse meine Mühe nicht umbsonst sein; so baldt ein Schif geht, wil ich ihm mit Weitzen Mehl versehn; so er verlangt dass zu haben, womit ehr den Corallen die Tinctur extrahieren kann und in eine Massa als Pillen gebrauchen kan, wil ich ihm senden, was ehr von chymischen Medicamenten verlangt. Schreibe ehr mihr, weihl ich ohn dem hier eine Collectio chymicorum halte; muss ich sie doch machen und stehn mir übern Halse. Wil mihr der Herr eine kleine Probe von seinem Feuer schicken, nehme ichs zu Dank an und ich erwartte des Herrn Antwort und Communication. Befehl ihm sambt seiner Liebsten und kleinen Dochter in den Schutz des Höchsten... P.S. Der Herr Doctor schreibe mihr, was ich ihm von dem Provit, den ich mache, geben sol, oder wenn ich mehr mache, als so und so vihl, wie ihm deucht, dass ehr mit diesen wil vergnüget sein und wan ich et wem bei einem Grossen Herrn kohme, da ein Stück Gelt vohr die Communication kriegen könnte, die dem Herrn anständig und ich möchte wegen Ablegenheit seinen Consens nicht kriegen können, was ehr haben wil, dass ichs frey meines Eydes und Gewissen ohnbeschedigt thun mach, nehmlich wenn ichs einen communicirt. So ichs diese Post kriege und so vil davon gemacht als mir deucht, so wil ich in Persohn nach Florentz uns beiden zum Nutz damit; aber der Herr seh sich vohr, sehe nu wenigs nicht an und gebe nicht mehr hiervon; schreibe mihr der Herr cito, ich will allen den nachkommen, denn in Deutschland verlohnt es der Mühe nicht." [**]

However, *Brand* does not seem to have been inclined to give *Kunckel* further information regarding the preparation, in spite of the latter's promises. He had already heard the essential facts – indeed, he expresses in no uncertain terms his concern that Brand might tell others just as much – and deviated from *Brand*'s procedure only in that he mixed the urine extract with sand prior to distillation[40]. He than met with success. Such a practice, however, would seem to have been common enough in those days, for *Robert Boyle* adopted it immediately[41] once he had heard from

[36] *J. H. Cohausen*: Lumen novum Phosphoris accensum. Amsterdam 1717, p. 163.

[37] Cf. ref. [1], p. 93.

[38] Cf. ref. [18], p. 1196.

[*] "Salve! Most honorable Doctor, trusted and esteemed friend, you will no doubt remember our agreement, namely that you would send me the "lumen" in a glass. Now see that you get it into a suitable crystal glass and dispatch it soon, so that I can see it, for I have thought of something wonderful to do with it..."

[39] Cf. ref. [18], p. 1196.

[**] "I cannot say enough how pleased I was to receive your letter of June 3. In it I perceive your good will and can assure you that I will honestly keep that which I have sworn to you. I hope that you will give me your fire; the excuse that you did not dare to write it down should cause you no uneasiness. You should write it thus: You take the known material, so much, add another substance, and proceed thus; who will understand that ...? I bid you to trust me as a good friend, give it to no other people, and let me arrange the matter. If you tell it to me, then I – as sure as I wish to partake of God's grace – will behave in a manner such that you and yours will be grateful to me – but you must follow me unconditionally ... I possess a considerable amount of the known material; I have distilled it twice, but not obtained any fire. I ask you so that my efforts may not have been in vain. As soon as a ship departs I shall send you wheat flour. If you wish to have that with which you extract the tincture from coral and can make pills of the substance, then I shall send you all the chemical medicine that you desire. Write and tell me since I have here a collectio chymicorum as it is; I have to look after it nevertheless and it is beyond that which is sufficient. If you send me a small amount of your fire I shall gladly accept it. I expect to hear your answer and communication. I commend you and your dearest one and little daughter to the care of the Almighty ...

P.S. You should inform me how much I should give you of the profit I shall make; or if I obtain more then a certain sum you should tell me how much you require in order to be satisfied, likewise if I show it to an important man and can receive as much money for its communication as he deems fit, that without your consent, if I tell it to anybody I should like to do so while no longer bound by my oath and without hurting my conscience. When I have received this information by the next post and have done as much as I think proper, then I shall journey to Florence myself to our mutual benefit. But you should be certain that you give none of it to anybody else. Write to me soon and I will do so anyhow, because in Germany there is no use whatsoever."

[40] Cf. ref. [16], p. 25ff.

[41] *R. Boyle*: The Aerial Noctiluca, or new Phaenomena and a Process of a Factitious self-shining Substance. London 1680. – The Works of the Honourable Robert Boyle. New edition. Vol. 4, London 1772, p. 379–404.

Krafft, "...that at least the principle matter of his phosphorus was something that belonged to the body of man" [42] – without proceeding to make any claim to the discovery or rediscovery (thus *e.g. P. Walden* [15] still for *Kunckel* and *Boyle*), although he was the first to actually examine phosphorus closely and to find, *inter alia*, that "dry phosphorus" only luminesces in contact with air, whereas his predecessors had all spoken of an "eternal" light or fire. Moreover, *Boyle*'s procedure was the first to be published [43].

Krafft, whose name was also occasionally given to phosphorus, never made any claim to the first discovery or to any rediscovery himself. He was simply faster and more clever than *Kunckel* (and, of course, than *Brand*), from whom he first learned of *Brand*'s phosphorus in early 1676: He was able to start negotiations with *Brand* before *Kunckel* and "as he openly admitted, to purchase the art from *Brand* for money" [44]. It is doubtful whether he ever succeeded in the preparation himself; he used the samples he received as exhibition pieces and journeyed through various countries demonstrating them, together with other "phosphori", at Royal Courts and before Scientific Societies (as *Kunckel* also suggested to *Brand*), and advertised the "phosphorus" extensively in journals [45]. (The demonstrations at the Berlin Court, whose description by *Elsholz* represents the first publication on the new phosphorus, and also first gives this name to the new substance [46], at the Hanoverian Court where *Leibniz* was Hofrat, and before the Royal Society at London have already been mentioned.) Nevertheless, it was through *Krafft* that phosphorus became widely known – and it is indeed most fortunate that *Kunckel* and he ever came to know of its discovery (see below).

Although *Krafft* appears to have made no mention of the discoverer at Berlin, he named *Brand* as the discoverer at both Hanover – cf. *Leibniz*' letter of recommendation to the Royal Society [47] – and London [48]. And since even Kunckel did not dare to deny *Brand* all credit for the discovery, the latter became almost undisputedly [49] recognized as the discoverer of phosphorus in the late 18th century, when, for topical reasons (see below), interest in the history of the discovery was revived.

[42] Cf. ref. [41], p. 382.

[43] Cf. ref. [16], p. 27.

[44] *G. E. Stahl*: Experimenta, Observationes, Animadversiones CCC Numero, Chymicae et Physicae. Berlin 1731, p. 392.

[45] Cf. *G. W. Leibniz*: Sämtliche Schriften und Briefe. Erste Reihe: Allgemeiner politischer und historischer Briefwechsel, Vol. 2. O. Reichl, Darmstadt 1927, p. 392.

[46] *J. S. Elsholz*: De phosphoris quatour observatio. Berlin 1676, p. 1–6.

[47] Cf. ref. [18], p. 1197.

[48] Cf. ref. [41], p. 382.

[49] *H. E. Fierz-David* represents an exception among modern authors. In his 'Die Entwicklungsgeschichte der Chemie'. 2nd Edit. Birkhäuser, Basel 1952, p. 147 (1945, p. 146), he states: "His [*i.e. Kunckel*'s!] most important contribution was that he first [?] prepared elemental [?] phosphorus by ignition of evaporated urine with charcoal [?]. He [?] called the substance phosphorus ..."

Earlier attempts [50] to trace the discovery of phosphorus to a date previous to *Brand* and 1669, and even back to antiquity have been finally refuted by *Partington* [51] and *Weeks* [52].

Little is known about the discoverer *Hennig* (*Heinrich, Hennig*) *Brand* [53]; not even approximate dates are recorded for his birth and death. According to *O. Sperling*, he attempted, in 1688/1689: "bei Schipbek in dem Berge mit etzlichen Soldaten der Stadt, so er bedungen, zu graben nach einem allda verborgenen grossen Schatze, wovon er Bericht hatte bekommen, und hatte dazu von dem Herzog von Holstein *Christian Albrecht*, der sich zu Hamburg aufhielt, öfters und inständig darum angehalten, Zulassung erhalten ... Fing deswegen an zu graben mit Wünschelrute und anderem Zubehör und Zusehern aus der Stadt bei Tausenden ... Derselbe Chymikus schreibt ihm [d.i. sich] zu, dass er der erster gewesen, der ex spiritu urinae den Phosphor, wie es die Chymiker nennen, wann der Spiritus geschüttelt, feurig scheint, zuwege gebracht ..." (September 1688) [54] "Es hatte ein Schmied einige Nachricht davon erhalten, dass vor Jahren ein Fuhrmann, der Sand führte, wie er am selben Ort gegraben, einen Beutel mit Dukaten gefunden, welches ihnen anzeigen machte, daß noch mehr vorhanden sein müsste, und gruben darauf fort, weil der bemeldete Chymikus und der Schmied in Gesellschaft mit einander getreten, da der dann der Chymikus *Brand*, der sich Doctor nennen liess, bisweilen mit seinem sammeten Rock die Zeche an den Wirth bürgen werden müssen, und auch von den Soldaten, die gegraben hatten, und ihre Bezahlung von ihm nicht erhalten können Schläge mit Scheltworten hat bekommen" [*].

[50] Cf. [16], p. 2–6; *G. Landgrebe*: Über das Licht. Marburg 1834.

[51] *J. R. Partington*: A history of Greek Fire and gunpowder. Heffer and Sons, Cambridge 1960.

[52] *M. E. Weeks*: Discovery of the elements. 7th Edit., J. chem. Educat., Easton, Pa. 1967.

[53] The most important references are [3] (p. [35]), [1], where [20] is essentially corrected, as well as the correspondence *Brand-Leibniz-Krafft-Kunckel* [18, 19]; the best summary is to be found in [16], p. 9–12 (to which the reader is referred for detailed references).

[54] *O. Sperling*: Hamburgische Chronik (manuscript Royal Library Copenhagen), Vol. VI, p. 329. Cited after *R. Benzian*: Henning Brand. Mitt. Verein für Hamburgische Geschichte *8*, 253 (1902/1904), p. 267ff.

[*] "... to dig for a great treasure of which he had heard near Schipbek in the mountain with some soldiers of the town who he had contracted, and for which he had obtained permission after frequent and urgent application, from the Duke of Holstein, *Christian Albrecht*, who stayed at Hamburg ... Began digging with the aid of a divining-rod and other equipment, and spectators from the town of Hamburg by the thousand ... The same chymist claims to be the first to have obtained ex spiritus urinae, phosphorus, as it is called by chemists, because the spirit appears fiery when shaken ..." "A certain smith had heard that many years ago, a certain carrier, who transported sand, had dug at the same spot and found a purse containing ducats, which made them think that more must be hidden, and continued digging, because the above chymist and the smith had become acquainted, and since the chymist *Brand*, who called himself doctor, had to surrender his velvet coat to the host as surety for the bill and was unable to pay the soldiers who had dug, he received blows and curses." (Spring 1689 [55]) – In 1710, *Leibniz* wrote [56]: "Indeed, as I have heard, he was still alive in the year 1692, when these [*i.e. Homberg*'s] stories were being circulated, and I do not know to this day whether he is dead." – A search in Hamburg archives has so far brought no further details to light.

It is not even known whether *Brand* was born at Hamburg; all we can be certain of is that he worked in this city between 1669 and 1692. The fact that he used low German in common speech, as *Kunckel* disparagingly reported, certainly suggests a North German origin [57]. As a young man *Brand* served as an officer who had worked his way up from humble beginnings. During the period given above he was married to an originally wealthy widow, who had a son by her first marriage and later bore *Brand* a daughter. He practised as a physician and dealt in chemical medicaments, most of which he probably made himself (cf. *Kunckel*'s letter cited above). Although he called himself doctor medicinae, and is also referred to as such by *Leibniz* and in the apparently friendly letters of *Kunckel*, it is doubtful whether *Brand* had been able to complete a course of study in medicine. In any case, his name is not to be found in the list of members of the Hamburg Collegium medicum [57]. Some doubt also surrounds where *Brand* had obtained his extensive "chemical" and metallurgical knowledge, to which *Leibniz* attests in high degree, and which – if we ignore *Brand*'s own statements – also *Krafft* and *Kunckel* were compelled to recognize.

From *Leibniz*' reports to the Duke of Brunswick-Lüneburg and from the correspondence between him, *Brand*, and *Krafft*, we come to know *Brand* as a readily excitable, but also easily soothed personality, as a person who was full of often adventurous plans and ideas, of which he often failed to realize the significance and value [57]. *Leibniz* considered him to be the right man to carry out the process of the "secretum" twenty times a week in the smelting works of the Harz mountains, and in a report to the Duke characterized him in the following way:

"Dr. *Brand* is unable to judge his own capabilities, or to assert himself. Not that he does not often indulge in fanciful and conceited talk, but, like all men, he has a character of his own. He is easily led, lacks a developed power of judgment, and leads a disorderly life, but he is quick to act and an extremely skilled worker ... I have often noticed that he makes a great bustle about trivialities but makes little fuss about things that deserve it. He is always looking for great secrets and fanciful things instead of realizing that he could live better from that which he has already accomplished."

These words seem to portray *Brand*'s character admirably; in any case, other reports – such as the futile treasure hunt involving tremendous effort but no money, so that after the failure of the venture the contracted soldiers had to make up for their trouble with blows and curses – and statements made by *Brand*, of which *Leibniz* could then have had no knowledge, harmonize with this picture. In general, it appears that *Brand* was always short of money – his wife's capital was soon spent on alchemical experiments; *Leibniz* promised to pay his debts to the City of Hamburg – and that in spite of his large income as physician, which still remains when deductions are made from the figures contained in his letters to *Leibniz* since they may represent an attempt to obtain more money for his household at Hamburg and as compensation for loss of income during his visit to the Duke at Hanover.

During an official journey to Hamburg, *Leibniz* had visited *Brand* and made an agreement, subsequently endorsed by the Duke, that the latter tell *Leibniz*, who was committed to secrecy, about the preparation of phosphorus and continually keep him informed regarding his chymical experiments. *Leibniz* then insisted that *Brand* immediately accompany him on the return journey to Hanover, since there was a very real danger that *Johann Joachim Becher* (1635–1682) would try to secure *Brand*'s information for a better price. In fact, *Becher* was most interested in *Brand*'s alleged "secretum" for the transmutation of silver to gold, which *Leibniz* also wished to reserve for his Duke, should it prove successful. By various intrigues he had been able to keep *Brand* unaware of *Becher*'s offer. It is therefore understandable that *Brand* felt cheated – for a second time after his discovery of "cold fire", whose value he had not recognized, had been commercialized by others – when he eventually heard of the offer, and from then on his relationship to *Leibniz* became cooler and cooler, particularly when, after the death of Duke *Johann Friedrich*, the Hanoverian Court failed to fulfil its part of the agreement and various other promises.

Meanwhile, at Hanover, *Brand* set about the preparations for the large-scale manufacture of phosphorus from human urine, to be provided by the local garrison (there are reports of some 100 tons, corresponding to about 13140 liters), and told *Leibniz* the secret of the process, as agreed. When the phosphorus had been made, *Leibniz* immediately sent a sample to *Christian Huygens* at Paris and wrote the following words to the Duke of Chevreuse in December 1778: "At last I have obtained the procedure; I am now the fourth to possess it."

Brand remained at Hanover for five weeks and on his return he complained about the slow and incomplete payment he had received. Nevertheless, he made a second visit in the latter half of the year 1679. However, the planned manufacture of large quantities of phosphorus, for which *Brand* had taken his stepson as assistant, does not appear to have taken place: *Brand* soon fell ill and spent two months recovering at Hanover. The death of the Duke on December 28, 1679, appears to have deprived him completely of any reward for his efforts, for in a letter of April 23, 1682, *Brand* demands the remaining money owing to him, presumably once more in vain. – The Court had run into financial difficulties, and *Brand* had suffered yet another disappointment.

3. The Material Discovered

In his 'Historia' [58] *Leibniz* reports on the motivation for the discovery of 'Phosphorus igneus': "During his studies *Brand* came across a procedure, published in a

[55] Cf. ref. [54], Vol. VI, p. 382.

[56] Cf. ref. [1], p. 93.

[57] Cf. *H. Schimank*: Zur Geschichte der exakten Naturwissenschaften in Hamburg. Naturwiss. Verein in Hamburg, Hamburg 1928, p. 63.

[58] Cf. ref. [1], p. 93.

printed work, for the preparation of a certain liquor from urine by means of which pieces of silver could be matured to gold. On following the same procedure he discovered his phosphorus." In a letter of April 11, 1682, he suggested that the said book was one of the works of *Franz Thomas Kessler*[59]. However, *Peters*[60], supposes it to have been 'Alchimia Nova' by *H. Binelli*, a German translation of which had appeared in 1603. Even though this question will probably never be answered unequivocally, the text of *Binelli*'s book makes it quite clear to what end *Brand*'s investigations were directed and what he believed he had found[61]:

"... daß die Alchimy jhren Vrsprung auß keinem Stein oder Metall haben könne. Sintemahl solche Sachen nicht gebähren oder jhres gleichen zielen ... es könne die Alchimy weder aus einem vnuernüfftigen Thier, noch auch auß jrgend einem Gewächse oder Kraut ... herkommen vnd entspringen, so wende dich zu der Empfängnung vnd Geschöpff des Menschen selbst, ... so wirst du befinden, daß der Mensch ein gebährender Anfang oder Vrsprung auch der Alchimistischen Materien vnd Steine sey: Denn er ist ein vegetalisch, rationalisch vnd mineralisch Thier vnnd aller Elementen theilhafftig, vnnd hat Mineras vnd viel Poros oder Schweißlöchlein in sich. Geschicht dir aber mit dieser Antwort nicht genug, so hör vnnd merke für das ander, was die alte Philosophi sagen, daß nehmlich der Mensch die kleine Welt sey: Ist er nun die kleine Welt, so muß er auch alles dasjenige in jhme haben, was die andere grosse Welt in jhr hat, wiewol ein jedes in geringer Mänge. ... frag in diesem dein eygen Gesicht, das wird dich berichten, daß sich mineralische Sachen in deß Menschen Leibe finden, vnnd daß der Mensch zweyerley Potestates oder Vermögen in jhm habe als erstlich einen Samen ... Die andere Krafft aber ist etwas geringer ... als da sind Harn, Schweiß, Koht vnd dergleichen ... Ist demnach der Mensch ein solcher Anfang vnd Geschöpff, aus welchem die Steine vnd Materien der Alchimy jhren Vrsprung her haben ... Wenn man den Harn ansihet, so bekompt derselbige nicht allein für sich selbst vnd von Natur die Härte vnd Natur eines Steins, sondern kan auch durch die Kunst dazu gebracht werden: Kan demnach dasjenige, aus welchem die Alchimy herkompt vnd entspringt, sehr wol seyn. Vnd damit du dessen, daß dem nemlich so sey, noch mehr versichert werdest, so erjnnere dich dessen, so die Philosophi fürgeben, daß nehmlich jhr Stein in der kleinen Welt entspringe .. Sprichstu aber, ... ich ... kan mich aber nicht genugsam verwundern, woher doch dem Harn solche große Kraft ... komme: darauff gib jch dir zur Antwort. Das eben der Harn diese Natur vnd Proprietet oder Eygenschafft hat, daß er zu einem Stein wird. Vnd zwar so sagen die Skribenten, es müsse ein solcher Harn, welchen man hierzu gebrauchen wil, einer reinen Natur vnd ohn allen Schweiß seyn, vnd derowegen von einem jungen gesunden Knaben, so mit den besten Speisen vnd gutem köstlichem Wein vnterhalten vnd ernehret worden vnd sich der Vnkeuschheit weder in der That noch auch mit den Gedanken jemals beflissen, genommen werden."[*] (The generative power must be preserved in its entirely!)

[59] Cf. ref. [45], Vol. 3. Koehler u. Amelang, Leipzig 1938, p. 529 (Letter to *Ch. Philippi*). *Kessler*'s works are listed by *F. Ferchl*: Chemisch-Pharmazeutisches Bio- und Bibliographikon. Published for the Gesellschaft für Geschichte der Pharmazie, Nemayo, Mittenwald 1937, p. 271.

[60] Cf. ref. [19], p. 88, note 6.

[61] *H. Binelli*: Alchimia Nova, das ist die güldne Kunst; verdeutscht von *P. Uffenbach*. Frankfurt a. M. 1603, p. 3ff.

[*] "... that alchemy cannot have its origin in any stone or metal. Since such things cannot give birth and produce their equal ... alchemy cannot arise ... from an irrational animal or from any plant or herb, therefore turn to that which man creates with his body, ... then you will recognize that man is a procreating genesis or origin also of alchemical material and stones; for he is a vegetal, rational, and mineralistic animal and can partake of all elements, and he has mines and many pores or small sweat holes in his body. If this answer should not satisfy you, then listen and note what the philosophers of old said, namely, that man is the microcosm: Now if he is the microcosm then he must contain everything that the macrocosm contains, but in smaller amounts. ... ask yourself, then you will see that minerals are to be found in all men, and that man possess two kinds of potestas or strength: the first is his sperm ... the other strength is somewhat weaker ... that is urine, sweat, feces, and suchlike ... Man is therefore such a beginning or such a creature, from which the stones and materials of alchemy can arise ... If one considers urine, not only does it turn spontaneously and by nature into the hardness and nature of a stone, but it can also be induced to do so by the art: therefore it can well be the source and the origin of alchemy. To provide further support for this concept, keep in mind that the philosophers are of the opinion that their stone originates in the microcosm ... If you should wonder whence urine has its great power, I offer the answer that urine is capable of being transformed to a stone. And indeed the scribes say that the urine used must be a suitable one, of a pure nature and containing no sweat, and therefore from a young, healthy boy, who has been nourished with the best food and good wine, and chaste in thought and deed."

Concepts of the human microcosm as a miniature embodiment of the macrocosm are extremely old. Since late antiquity, *i.e.* from the very beginning, they played an important role in alchemical thought. The fact that they had again assumed a particularly important place in alchemical thought in the 16th and 17th centuries is shown by *Boyle*'s reaction to *Krafft*'s intimation that the starting material for 'cold fire' was of human origin (see Section 2): He immediately started with urine.

But is it not just this general intellectual situation of alchemy that throws light on *Brand*'s relationship to the art and on his chemical aptitude? Was not he, as a crass outsider, actually the only person to have successfully carried out the generally known and recommended (but probably only rarely actually performed) process of extraction from urine until he had indeed obtained a substance possessing wonderful properties? Or was his lack of prejudice concerning the properties of the 'secretum' obtained an additional factor? The alchemists expected to find a "black" substance, the unfermented 'prima materia'; and for the 'spagyric art', 'fire' was only an external conditio sine qua non for the chemical processes that was not permitted to come into direct contact with the starting materials and intermediates, which were sealed off 'hermetically'. Or, was it merely the desperate situation arising from his permanent financial embarrassment that compelled *Brand* to invest such an uncharacteristic measure of patience in the preparation of the desired agent for the transmutation of silver to gold, and to place such faith in the old text. It was probably the fortunate combination of all three factors that actually led to the discovery.

It thus also becomes understandable why *Brand* kept his discovery secret for such a long time. The 'phosphorus' – in neither the liquid nor the solid form – was not the 'secretum' itself, but merely an important component or starting material, which he occasionally showed only to close friends. In 1677 *Brand* was still convinced that he would soon possess the 'secretum', and even two such important men as *Leibniz* and *Becher*, whose preliminary work later formed the

basis of *G. E. Stahl*'s phlogiston theory, opened negotiations to obtain this agent for their respective masters.

It is therefore perfectly feasible that earlier alchemists had already found the 'cold fire' – a procedure given by *Paracelsus* (1493–1541), for example, appears to suggest that this was the case [62]. Even *Brand*'s discovery only became known by a fortunate combination of circumstances.

Brand himself never published any reports concerning his phosphorus, and none of his remaining letters give away any information regarding the method of preparation. However, he did tell *Leibniz* of the preparation as agreed, and the latter successfully carried it out together with a number of assistants: ... *Brand* "honestly informed me of his process; for, with my assistants, I have repeated in another laboratory all that he accomplished" [63]. It has already been mentioned that in December 1678 he boasted to the Duke of Chevreuse of being the fourth (after *Brand*, *Krafft*, and *Kunckel*) to possess the procedure for the preparation of phosphorus. It is therefore a reasonably safe assumption that the procedure which he sent to *Ehrenfried Walter Freiherr von Tschirnhaus* (1651–1708), who was then in Paris seeking admission to the Academy, in an undated letter of the year 1682 was the very same recipe that he had received from Brand. The letter begins with personal and mathematical details and continues [64]:

"Phosphori Process kommt hierbey. Solchen werde, so lange M. Hr. mir nicht den ausgang seiner sach melde, nicht communiciren, zumahlen sie mir noch nicht geschrieben, was sie mir vor curiosa experimenta dafür communiciren wollen. M. Hr. wird solche doch auch leicht erfahren, und werde ich sie also durch ihn bekommen, hat also M. Hr. vom phosphoro nach seinem belieben zu disponieren. Nur dieses muss bekennen, dass das phosphorum zu machen, eine ziemlich beschwehrliche arbeit, und muss man sonderlich bey der letzten arbeit zusehen, dass die retorte nicht springe. Des Mons. *Boyle* ist etwas kürzer, aber wie ich aus seiner Beschreibung sehe, so fehlet er ihr bisweilen, gibt auch keinen so starken phosphorum, und überdies so ist er nicht instructif, denn er weiset nicht analysin subjecti et ex qua ejus parte potissimum veniat phosphorus. Zweifelsohne ist M. *Boyle* darauff gefallen, weil ihm der phosphorus imperfecte communiciret worden. Schicke hiermit beyde processus, sowohl wie ich es gemacht, als wie M. *Boyle*.

Composito des Feuers oder pyropi. Habe genommen urin so eine zeitlang gestanden, etwa eine tonne (wiewohl ich zweifle, obsolche fermentation oder putrefaction nöthig sey, weil mein Diener in Copenhagen den phosphorum noch selbige woche, als er hinkommen, gemacht), kochet es ab bis es beginnet dick zu werden, wie ein dicker sirup, alsdann thut man diesen dicken urin in eine retorte, lässet das phlegma und volatile vollends wegrauchen, und wenn rothe tropfen zu kommen beginnen, leget man einen recipienten vor, und empfängt darinn das oleum urinae. Alsdann schlegt man die retorte in stücken, darinn findet man ein caput mortuum, dessen unter theil ist ein hartes salz, so hieher nicht dienet, das obere theil ist eine schwarze lückere materi, die hebt man auff. Das oleum urinae thut man wieder in eine retorte und ziehet alle feuchtigkeit stark davon ab, so findet man in der retorte eine schwarze lückere materi der ietzgedachten, so in voriger retorte gewesen ganz gleich. Thut sie zusammen und treibt das feuer daraus folgendermassen. Nim eine guthe steinerne retorte, so kein stübgen nicht hält, darin thue etwa 24 Loth von der schwarzen materi oder capite mortuo oleoso, lege einen ziemlichen gläsern recipienten vor, so wohl verlatirt, und treibs also in freyen feuer, doch erstlich gelinde bis die retorte wohl glüet, treibs wohl 16 stunden lang, die letzten 8 stunden aber gar stark. Es kommen bald weisse Nebel oder wolcken und sezet sich wie ein schlammig oel zu boden. Gehet auch wohl etwas von einer materi mit über, die sich ganz hart an das glas anleget, ist wie ein Börnstein, darinn bestehet die beste krafft. Im ... destilliren ist der recipient ganz hell, und leuchtet im finstern. Was übergangen, ist alles leuchtend, doch das siccum mehr als das humidum. Hieraus ersiehet man, dass das feuer stecke in dem capite mortuo oleoso ...

Ich weiss keinen process, der auff die vulgata Chymicorum principia, sal, sulphur und mercurium, besser quadrire, als die compositio dieses feuers oder pyropi, denn dieses feuer komt eigentlich nicht aus dem sale fixo, noch aus dem volatili oder Mercuriali, sondern aus dem medio oder oleo vel sulphure. Und deucht mich, dass dieser process kein geringes licht gebe ..." [*]

[62] *Paracelsus*: Sämtliche Werke. Nach der zehnbändigen Huserschen Gesamtausgabe zum erstenmal in neuzeitliches Deutsch übersetzt ... von *B. Aschner*, Vol. 3. G. Fischer, Jena 1930, p. 18; cf. *O. C. de C. Ellis*: A history of fire and flame. London 1932, p. 24.

[63] Cf. ref. [1], p. 96.

[64] *G. W. Leibniz*: Mathematische Schriften, Vol. 4. G. Olms, Hildesheim 1962 (Halle 1859), p. 496 and 498.

[*] "The process for the preparation of phosphorus is enclosed. I shall not communicate it until you have informed me how your matter has gone, particularly as they have not yet written to tell me what curious experiments they wish to exchange for the communication. You will, however, also have no difficulties in obtaining such experiments, and if I learn of them from you then you will have phosphorus at your disposal. It must, however, be said that the preparation of phosphorus is rather difficult and that towards the end one must be particularly careful that the retort does not crack. The procedure of Mr. *Boyle* is somewhat shorter, but as I see from his description it has sometimes been unsuccessful and, moreover, it has not produced a very strong phosphorus. In addition, his description is not instructive for he does not order analysin subjecti and he does not know from which part of it the best phosphorus originates. This is undoubtedly due to the fact that he has only been imperfectly told of the preparation of phosphorus. Herewith I send you both procedures, not only that which I have used myself but also that of Mr. *Boyle*.

Composition of the fire or pyropus. Take approximately a full ton of urine that has stood for some time (although I doubt that such fermentation or putrefaction is necessary, for my servant has prepared phosphorus within a week of his arrival in Copenhagen), boil it until it begins to thicken, like a thick syrup, then place this thick urine in a retort, allow it to phlegm and the volatile part to vaporize, and when red drops appear a receiver is placed in front of the retort and the oleum urinae is collected. The retort is then broken into pieces. One finds a caput mortuum in it, the lower part of which is a hard salt that cannot be used, the upper part is a black loose material which one keeps. The oleum urinae is again transferred into a retort and all moisture is vigorously removed, one then finds a black loose material in the retort which looks just like that in the previous retort. Both are united and the fire is driven out in the following way. Take a good stone retort that has been very well cleaned, fill it with about 24 Loth of the black material or caput mortuum oleosum, place in front of the retort a suitable glass receptacle that is well stoppered, and heat over an open fire, gently at first, until the retort glows; heat for a total of 16 hours, and fiercely for the last 8 hours. White smoke or clouds soon appear and a kind of muddy oil deposits at the bottom. Some material also distills over which strongly adheres to the glass, it is like amber and that is the best material. On ... distillation the receptacle is very bright and shines in the dark. All that has distilled over shines, the dry part more than the moist part. One can thus see that the fire is in the capum mortuum oleosum ...

I know of no process that better quadrates the general principles of the 'chymists' – sal, sulphur, mercurium – than the composition of this fire or pyropus, for this fire does not come from the sal fixum or from the volatile or mercuriale, but from the medium or oleum vel sulphur. And it seems to me that this process gives a good light ..."

Robert Hooke (1635–1703) later published a far more complicated procedure "Phosphorus Elementaris, by Dr. *Brandt* of Hamburgh" [65], in a form that could hardly have originated from *Brand*. It is also uncertain how *Hooke* could have learnt of the method from *Brand*. It is in fact one of the many procedures to appear in the early 17th century subsequently ascribed to the discoverer of phosphorus by *Hooke*.

It has already been mentioned that *Brand* called the substance he discovered in urine "cold fire" or just "my fire". He clearly thought that he was in possession of elemental 'fire', one of the four Aristotelean 'elements' (earth, water, air, and fire); an assumption confirmed by his use of the alchemical symbol for 'fire' (Δ) in his letters. The term employed by *Hooke* "phosphorus elementaris" (presumably: "bearer of elemental light"), which has a very different meaning from "elemental phosphorus" in the sense of the later 'chemical' elements of the 19th century, is also suggestive of a similar interpretation.

Other early names are: Phosphorus fulgurans (*Elshloz*, *Kunckel*), Ph. igneus (*Leibniz*, *Boerhaave*), Ph. mirabilis or Wunder-Licht (miraculous light) (*Kunckel*); Lumen constans (*Kunckel*, *Elsholz*), L. perpetuum (*Kirchmaier*); Lux condensata (*Sturm*), Ignis perpetuus (*Krafft*), feu corporel (*Leibniz* in a letter accompanying the first sample he sent to *Huygens* [66]), Noctiluca constans (*Kirchmaier*, *Cohausen*), Noctiluca aerea (*Boyle*), Pyropus (*Leibniz*), *etc.*

All these names show that *Brand*'s discovery was regarded as a kind of light or fire material, or at least a "bearer of light" or "of fire". Even after *Stahl*'s proposal of the phlogiston theory (1703), *Nicolas Lémery* (1645–1715) 'pensionnaire chimiste' of the Paris Academy since 1699, wrote the following lines in his 'Muthmassungen und Betrachtungen über die Feuer- oder Lichtmaterie' [67]:

"Die Feuermaterie ist das vorzüglichste und mächtigste Auflösungsmittel irdischer Körper. — Man muß zugeben, daß sie der wahrhafte Stoff der Wärme, des Lichts und selbst der Flüßigkeit oder die Ursach der Schmelzung der mehresten irdischen Körper sey, die ohne diese Materie immer vest bleiben würden. Sie ist aber nicht immer so häufig da, oder sie trifft nicht immer Körper an, die ihr so wenig Widerstand leisten, daß sie dieselbe zum Fließen brächte, ja, man bemerkt oft, daß sie, anstatt diese zu schmelzen oder sie in der Flüssigkeit zu erhalten, die sie ihnen anfänglich mitgeteilt hatte, sich an dieselben hängt, und darinn so eingewickelt wird, daß sie eingekerkert zurückbleibt, und nicht eher heraustritt, als bis eine äußere Ursache ihr zu Hülfe kommt, und die Zellen, worinn sie zurückgehalten wurde, öfnet.

Hierbei ist ein doppelter Umstand zu bemerken, daß sie nämlich 1) manchmal das Gewicht der Körper, worinn sie enthalten ist, merklich vermehrt [!]; und daß sie 2) während der ganzen Zeit ihrer Einkerkerung doch die eigenthümlichen Eigenschaften der Feuermaterie behält, die sie deutlich äussert, so bald sie frey wird ... Spießglaskönig, Bley, Zinn und selbst Quecksilber wiegen nach der Verwandlung in Kalk mehr, als im metallischen Zustande, ob gleich viel von ihnen bey der Operation verflüchtigt wird. Da nun die Feuermaterie sie in den verkalkten Zustand gebracht hat, soll man ihr nicht auch das vermehrte Gewicht zuschreiben? ... Unter allen Körpern, worinn die Feuermaterie am losesten eingeschlossen ist, sind die Phosphoren. Man braucht sie nur ans Licht zu stellen, da sie sogleich neue annehmen, die die erstere in Bewegung setzt. Es sind Lichtschwämme, die es eben so leicht von sich geben, als sie es annehmen ..." [*]

This view was destined to persist in a more or less similar form for a considerable time; even towards the end of the 18th century yellow phosphorus was still regarded merely as a particularly striking example of a whole series of "phosphorus", of "light (or fire) bearers" or "light imbibers", which differed from the others in that it did not have to be first exposed to light or fire in order to luminesce, as *Leibniz* put it.

As late as 1790 the following description appears in *Gehler*'s 'Physikalisches Wörterbuch' under the heading 'Phosphorus' [68]:

"According to its entymological meaning, the name phosphorus (light bearer) applies to any body that luminesces in the dark. However, the sun, the fixed stars, and burning or glowing bodies, whose luminescence is an everyday phenomenon, are excepted, and the name phosphorus applied only to the other substances that luminesce of themselves, whose light in the dark belongs rather to the rare and unexpected phenomena. Such substances are either natural or artificial phosphors. A number of the natural ones are considered under the heading 'luminous bodies'; the artificial phosphors therefore represent the main subject of this article".

The enumeration starts off in chronological order, beginning with Bologna phosphorus (BaS), whose discovery is incorrectly cited as having occurred in 1630 – it is first mentioned by *Julius Caesar la Galla* ('De Phaenomenis in Orbe Lunae'; Venice 1612), and a detailed description was given by *Fortuno Liceti* ("Litheophosphorus, sive de lapide Bononiensi'; Udine 1640) and *Athanasius Kircher* (Magnes, sive de arte magnetica ...'; Cologne 1643, as well as 'Ars Magna Lucis et Umbrae ...'; Rome 1656); the discovery occurred between 1602 and 1604, and is attributed to the Bolognese shoemaker *Vincenzo Cascioroli* [69]:

[*] "The fire material is the most powerful solvent for earthly substance – One has to admit that it is actually the substance of heat, of light, and even of liquid or the cause of the melting of most earthly substances, which, without this material, would always be solid. It is not, however, always present in such a degree, or it does not always find substance which offer so little resistance that they are made to flow; moreover, one often notices that, instead of melting these bodies or keeping them liquid as in the beginning, it attaches itself to them and becomes so intimately mixed with them that it remains imprisoned within them and cannot be freed until an external cause assists and opens the cell in which it is held back.
Two things are to be noted, namely that the fire material 1) sometimes increases considerably the weight of the bodies in which it is contained [!]; and 2) retains the properties of the fire material which it clearly exhibits when it is freed, for the duration of its imprisonment ... antimony, lead, tin, and even mercury, weigh more after calcination than in the metallic state, although large amounts of them are volatilized during the operation. Since the fire material transformed them to their calcined state, why should one not also attribute the increase in weight to it? ... The phosphors belong to the substances in which the fire material is most loosely bound. If they are exposed to light they immediately take up fresh fire material, which sets the confined fire material in motion. They are light sponges which release light just as readily as they absorb it ..."

[65] *Robert Hooke*: Philosophical Experiments and Observations of the late eminent Robert Hooke, publ. by *W. Derham*. London 1726, p. 178–180.

[66] Oeuvres complètes de Christiaan Huygens ... Tome VIII. M. Nijhoff, La Haye 1899, pp. 214–218; Letter No. 2192 of September 8, 1679.

[67] After the translation in ref. [6], p. 34–39. (Hist. de l'acad. royal des sciences, anné 1709. Amsterdam 1711).

[68] Cf. ref. [7], p. 475.

[69] *J. R. Partington*: A history of chemistry, Vol. 2. MacMillan and Co., London 1961, p. 334ff.

"It became luminous on exposure to both sunlight and candles, but not to the light of the moon or of another phosphor ... This discovery naturally led to the corpuscular concept of light, which not long afterwards became the basis of *Newton*'s theory of light. Here one saw, as it were, bodies, which attracted light and re-emitted it, light imbibers or light magnets (corpora lumen bibentia), which names have also been adopted" [70].

The second "phosphorus" to be dealt with by *Gehler* is *Balduin*'s phosphorus, which was first reported on by its discoverer in 1674 (see Section 1); he then goes on to discuss *Homberg*'s phosphorus ($CaCl_2$) and a series of other "artificial" phosphors, *i.e.* phosphorescing substances, before he comes to "*Kunckel*'s or urine-phosphorus".

The Bologna phosphorus and *Balduin*'s phosphorus (ignited calcium nitrate) indeed created great excitement in the scientific world and stimulated the search for other "phosphoruses". For example, *Homberg* had studied the former in Italy and as soon as he heard of *Balduin*'s discovery he payed the Saxon magistrate a visit at Grossenhain. In continuation of his journey he came to Berlin, where he met *Kunckel* who told him about another new phosphorus, *i.e.* *Brand*'s 'cold fire', and gave him a sample. *Kunckel* himself reports that a few weeks after his having become acquainted with *Balduin*'s discovery and been given a small sample, he was demonstrating the same during a visit to Hamburg when he heard that a Herr *Brand* of Hamburg had also discovered a luminous substance [71]. His informant was *Peter Hessel*, who was preacher at the Hamburg plague spital from 1670 to December 26, 1677, and apparently one of the few friends to whom *Brand* had shown his "fire" – fortunately, as we can now appreciate; for it is only due to facts that *Kunckel* had learnt of *Balduin*'s phosphorus from the discoverers publications and had been able to secure a small sample, that he demonstrated this at Hamburg, and that the versatile and literarily very active preacher, who had already seen *Brand*'s phosphorus, also happened to be present at the demonstration that *Brand*'s discovery ever came to *Kunckel*'s notice. He described what he had seen in a letter to his friend *Krafft* at Dresden and thus set in motion the course of events whose beginning are described above. *Brand* himself could never have dreamed of the significance of his discovery, or even of the possibility of a financial exploitation, so that we actually owe our knowledge of it to an unlikely combination of various chance circumstances – even though the discovery of the substance would certainly have followed later, and that in a less fortuitous and unconscious manner.

It has already been mentioned that "phosphorus" was originally prepared in one of two forms, either as a grayish or yellow solid or as "phosphorus liquidus" – *Elsholz* [46] reports *e.g.* that *Krafft* possessed samples of both kinds. Recent investigations on earlier reports and procedures have shown that the liquid form must have been a suspension of finely divided phosphorus in water (*Brand*, *Krafft*) or must have contained impurities. Such contamination, particularly with sulfur, would lead to a melting point below the normal temperature [72]. And the frequent contamination with sulfur, along with the ready combustibility (ascribed to the former principium sulphur), seems to have led to phosphorus being regarded as "a sulfur or a sulfurous substance" after the original idea of elemental light or fire had gradually been abandoned, or modified as in the above passage by *Lémery*, as a consequence of *Boyle*'s discovery that contact with air was an essential condition for luminescence of the solid material.

Homberg (1692), for example, like *Leibniz*, considered it to be the sulfurous principle of pre-phlogiston chemistry, when he said that phosphorus is the fattiest, *i.e.* the most combustible, part of urine, which is concentrated on a highly flammable earth.

Nevertheless, *Boyle* [73] had already recognized that the residue left by burning phosphorus possesses acid properties, so that it was only natural for *Stahl*, the founder of the phlogiston theory, to regard phosphorus as a compound of phlogiston and a concentrated acid. It is, however, remarkable that he was thinking, not of a specific acid, but of hydrochloric acid. Certain experiments by *Boyle*, which cannot be considered here, led him to this conclusion; he was so convinced of the correctness of his assumption that he, and his successors, considered any proof entirely superfluous. The deciding factor in the preparation of phosphorus was then thought to be the choice of the correct method of combining the phlogiston with the hydrochloric acid. Thus it can be read, *e.g.* in *Johann Juncker*'s widely read work 'Conspectus Chemicae' of 1730: "Phosphorus consists primarily of hydrochloric acid and phlogiston, which are bound most intimately by fire, and is therefore a kind of sulfur" [74]. The symbol $\frac{\triangle}{+}$, derived from the old symbol for the 'element' fire ($\triangle$), which *Brand* himself had used for phosphorus, found general acceptance (sulfur: $\frac{\triangle}{+}$).

It is clear that this theory made the preparation of phosphorus no easier. The only methods available were still the old, time-consuming, and inconvenient processes used by *Brand*, *Kunckel*, *Krafft*, and *Boyle*, which had undergone only slight modification. It was much simpler, although more expensive, to import phosphorus from England, where *Ambrose Godfrey Hanckwitz* (1660–1741), a pharmacist of Göthen in Anhalt who had emigrated to England and had become assistant to *Robert Boyle*, had set about producing phosphorus on a large scale. By closely guarding the secret of his preparation, which only became known sketchily in the 1730's, he had almost suc-

[70] Cf. ref. [7], p. 476.

[71] Cf. ref. [3], p. 660; also ref. [35].

[72] Cf. ref. [16], p. 29.

[73] *R. Boyle*: New Experiments and Observations, Made upon the Icy Noctiluca. London 1681/82: [41], p. 469–495.

[74] *G. J. Mielke* in *A. S. Marggraf*: Einige neue Methoden, den Phosphor im festen Zustande sowohl leichter als bisher aus dem Urin darzustellen als auch denselben bequem und rein aus brennbarer Materie (Phlogiston) und einem eigentümlichen, aus dem Urin abzuscheidenden Salze zu gewinnen. Translated from the Latin and French and edited by *G. Mielke*. W. Engelmann, Leipzig 1913, p. 45.

ceeded in establishing a monopoly for the production of phosphorus. The first records of shipments of phosphorus from London to Germany refer to the year 1685, and in the same year *Hanckwitz* advertised his product in London in the following way: "He sells Solid Phosphorus, wholesale, 50 s. an ounce, and retail, £ 3 sterling, the ounce." The prices remained at this level – in 1731 *Stahl* gives the price as 40 shillings the ounce in London and 32 Belgian guilders in Amsterdam –, and after the death of their father, *Hanckwitz*' sons were able to continue production for the same high profit [75].

It is thus also understandable that in 1736 the Paris Academy commissioned *Hellot*, *Du Fay*, *Geoffroy*, and *Du Hamel* to examine an offer of a more economical process for production of phosphorus which had been made by an unnamed foreigner, and that they subsequently bought the process. According to the report given by *Jean Hellot* (1685–1766) to the Academy on November 13, 1737, $3^1/_2$ pounds of calcined starting material gave 9 gros and a few grains of a phosphorus that was "at least as beautiful as that coming from England" [76]. The novelty of the process – and the only direct influence of the phlogiston theory on the preparation of phosphorus – was the addition of powdered charcoal *i.e.* "highly concentrated phlogiston", apart from sand or earthenware fragments (to ensure even heat distribution), to the starting material, putrified urine.

Then, a few years later, in 1743, *Andreas Sigismund Marggraf* (1709–1782) published a treatise in 'Miscellanea Berolinensia' which not only stripped phosphorus of its mystery, but also considerably simplified its preparation [77]. The author described what prompted him to undertake his experiments in the following lines [78]:

"Around the year 1734 I was fortunate enough to receive tuition by the famous and skilled *Henckel* [*Johann Friedrich Henckel*, 1679–1744] in Freiburg ... We frequently discussed phosphorus and its high price and exchanged our views on the matter, and on one such occasion he assured me that quite by chance, he had once produced phosphorus using only low heat," – the fierce heating, which had to be kept up for a considerable length of time had always caused difficulties – "while engaged in work on the mercurificatio [experiments to obtain 'mercurius' from metals]; he had already published this method in his 'Pyritologia' ['Pyritologia Oder Kiess-Historie'; Leipzig 1725]. I searched for the place and found on p. 1004, paragraph 14, the following words: 'Bleykalk mit Salmiak, Weinstein und altem Urin digeriert, endlich destilliert, giebt einen arsenikalischen Geruch, ja endlich einen schönen Phosphor' [*] ..."

Henckel provided him with further detailed information about the process, which was then studied systematically by *Marggraf* with the result that it became easier to prepare phosphorus, using less heat, and in greater yields when not only charcoal (as had become common practice since 1737), but also molten lead chloride [Hornblei] ($PbCl_2$ in the solid state), horn silver (AgCl), or cadmia fornacum (ZnO) was added to the concentrated urine. He studied which part of the urine actually gave rise to the phosphorus, or whether it might even have arisen from the substances added, particularly those containing chlorine, thus proving the conclusion reached by *Stahl* from his theory to be correct and phosphorus could be prepared without urine. During these studies he came across the "highly remarkable urine salt" ($NaNH_4HPO_4$), which had long been known under the name of sal microcosmicum (see above) and from which, in admixture with charcoal only, with charcoal and sand, or with charcoal and horn silver, could be prepared a "very beautiful and pure phosphorus". It should be only this salt that came into question for the preparation, as well as an "acid" obtained by ignition ($NaPO_3$), which is reduced to phosphorus by charcoal. Phosphorus could, however, be more readily obtained by reduction of the acid, upon which the urine salt is based, by charcoal.

According to this reasoning phosphorus was the compound of a specific acid, *i.e.* phosphoric acid, with phlogiston. As far as phosphorus was concerned, *Stahl*'s thesis had been disproved. Phosphorus, or rather phosphoric acid, had been recognized for the first time as a specific substance.

Carl Wilhelm Scheele (1742–1786) and his assistant *J. G. Gahn* (1745–1818) then discovered, in spring 1770 although it did not become known until 1774, the composition of "animal earth", *i.e.* of bone ash, and thereby found a new starting material for the preparation of phosphorus, before *Antoine Laurent Lavoisier* (1743–1794) opened, with his many experiments on the combustion of phosphorus and sulfur in 1772, "the crucial year", as it is called by *Henry Guerlac* in a recent presentation of *Lavoisier*'s experiments in this year.

On November 1, 1772, *Lavoisier* deposited a short, sealed note in the Academy, which was opened in May of the following year and published. The text runs thus [79]:

"il y a environs huit jours que j'ay decouvert que le Souphre en brulant loin de perdre de Son poids (en brulant) en acquieroit au contraire; Cest a dire que d'une livre de Souphre on pouvoit retirer beacoup plus dune livre dacide vitriolique, abstraction faitte de l'humidité de l'air. il en est de meme du phosphore Cette augmentation de Poids vient dune quantite prodigieuse d'air qui Se fixe pendant la combustion et qui Se Comnine avec les vapeurs.

Cette decouverte que j'ay Constaté par des experiences que je regarde Comme decisives m'a fait penser (ce) que Ce qui Sobservoit dans la Combustion du Souphre et du phosphore pouvoit bien avoir lieu a l'egard de tous les Corps qui acquier rent du poids par la Combustion et la Calcination et je me

[75] *M. Speter*, Chemiker-Ztg. *53*, 1005 (1929).

[76] Cf. ref. [16], p. 32.

[77] *A. S. Marggraf*: Nonnullae novae methodi Phosphorum solidum Tam ex urina facilius conficiendi, quam etiam eundem promtissime et purissime ex phlogisto et singulari quodam ex urina separato Sale componendi. Miscellanea Berolinensia *7*, 324 (1743). German version in ref. [74].

[78] Cf. ref. [77], paragraph 4; ref. [74], p. 4.

[*] "Massicot digested with sal ammoniac, tartar, and old urine, and eventually distilled, gives an arsenical odor, and finally a beautiful phosphorus."

[79] *H. Guerlac*: Lavoisier – The crucial year. The background and origin of his first experiments on combustion in 1772. Cornell University Press, Ithaca, New York 1961; p. 227ff. German version in ref. [81], p. 13.

Suis persuade que laugmentation de poids (de l) des chaux metalliques tenoit a la meme Cause. experience a Complettement Confirme mes Conjectures ... Cette decouverte me paroit une des plus interessantes qui ait ete faitte depuis *Sthal* [*Stahl*] et Comme il est difficile de ne pas laisser entrevoir a Ses amis dans la Conservation quelque chose qui puisse les mettre Sur la voye de la verité j'ay Cru devoir faire le present depost entre les mains de M. le Secretaire de lacademie (pour) en attendant que je rende mes experiences publiques [*]."

Two further notices dating from an earlier period have recently been discovered [80], which deal primarily with investigations on phosphorus, one written on October 10, and the other on October 20, 1772 ('Memoire Sur lacide du Phosphore et Sur Ses Combinaisons avec differentes Substances Salines terreuses et métalliques'). The paper 'On the combustion of *Kunckel*'s phosphorus and the nature of the acid formed by this combustion', which was read on April 16, 1777, possesses as great a significance as a step along the path to the further development of *Lavoisier*'s theory of combustion, as does the 'treatise on a particular process for the conversion of phosphorus into phosphoric acid without combustion' from the year 1780.

Yet in none of these reports does *Lavoisier* speak out against the phlogiston theory. However, he contends that the theory assumes unproven facts and expresses the hope that he will soon be able to provide experimental proof that combustion and calcination can be explained without the need for the assumption of a special basic substance such as phlogiston [81].

[*] "About eight days ago I discovered that sulfur does not lose weight on combustion but rather gains weight; that is to say, much more than a pound of sulfuric acid is obtained from one pound of sulfur, after deduction has been made for the humidity of the air. It is the same with phosphorus. This increase in weight is due to a considerable amount of air which is fixed during the combustion and combines with the vapors.

I concluded from these facts, which I have determined from experiments that appear decisive to me, that which is observed on combustion of sulfur and phosphorus might well take place with all bodies which gain in weight on combustion or calcination, and I have become convinced that the increase in weight on calcination of metals is due to the same cause. The experiment completely confirmed my supposition ... This discovery seems to be one of the most interesting since *Sthal* [*i.e. Stahl*]: I therefore believe to have acquired the priority of the same in that I place this in the hands of the Secretary of the Academy, where it should remain secret until I publish my experiments".

[80] Cf. ref. [79], p. 223–227.

[81] *M. Speter*: Lavoisier und seine Vorläufer. Eine historisch-kritische Studie. F. Enke, Stuttgart 1910, p. 12ff. (Special edition from: Sammlung chemischer und chemisch-technischer Vorträge, Vol. 15, Numbers 4–6.)

At this time, *Lavoisier*'s theory that a component of the air was responsible for all combustion and calcination had too many weaknesses, which he also recognized himself, for anyone other than he to be able to follow it. It seems, however, that it was precisely the combustion experiments with phosphorus and sulfur that were decisive for *Lavoisier*. Yet it was not until the discovery of the composition of water by *Henry Cavendish* (1731–1810), which came to *Lavoisier*'s notice in June 1783, that the theory received welcome confirmation, and was then, in 1789, brilliantly developed in 'Traité élémentaire de Chimie'. Rapidly accepted in France, the theory soon won general recognition by the chemists of Europe.

On the basis of this "antiphlogistic" theory, phosphorus was relegated to a simple, undecomposable substance, a chemical element. Thus, in 1795, *Gehler*, who as short a time ago as 1790 had been a convinced supporter of the phlogiston theory and had made just brief mention of *Lavoisier*'s work on phosphorus as a recent theory [82], had no alternative but to begin his remarks on phosphorus in a supplement to his dictionary with the words [83]:

"The name phosphorus has become reserved almost exclusively for *Kunckel*'s phosphorus or urine phosphorus, particularly since the antiphlogistic theory has come to regard it as a simple substance and has adopted a large number of derivations from its name in the nomenclature" ... It "has become an uncommonly important object in recent chemistry. The phenomenon of its combustion in atmosphere or dephlogistated air provides the antiphlogistic system its most important support, and proves with undisputable certainty that the basic part of the breath of life combines with the burning body on combustion ..."

Thus it took more than one hundred years for the material discovered by the Hamburg Chymist *Hennig Brand* to become the chemical element phosphorus. However, the credit for the discovery remains his; for while it is true that a science develops by continually wrestling with new interpretations from that which it observes, this is only made possible by the existence of a foundation established in history; and that stone provided by *Brand* was by no means unimportant. We can hardly reproach him for not realizing that his contribution would later assume a significant place in this foundation.

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[82] Cf. ref. [7], p. 483.

[83] Cf. ref. [7], Vol. 5, p. 708.