The Early History of Phosphorus.

The term phosphorus was formerly applied to any substance which was luminous, either after exposure to light or after the application of heat, and the "phosphori," which received so large a share of attention, had no connection with the substance now known as phosphorus, and should rather be regarded as the ancestors of the luminous paints of to-day.

The peculiar, light-emitting property of the phosphori, however, secured to them so great a popularity among the dilettanti that when the element was isolated it was sold at a fabulous price, and was regarded by many as an important step towards the discovery of the divine arcanum by which base metals could be transmuted into gold. The value possessed by the so-called phosphorus (a sulphide of barium) of Balduin in the seventeenth century is well shown in a letter from Christianus Adolphus Balduinus to Mr. Oldenburg, sent with a piece of "phosphorus" in a silver-gilt box for "His Majesty the founder of the Royal Society" (*Phil. Trans.*, 1676-7, vol. xi., No. 131, p. 788).

Although, with an unusual extension of the novelist's license, Charles Reade makes one of the characters in the "Cloister and the Hearth" use phosphorus in the fifteenth century, it was not until the year 1667, according to some authorities, or 1669, according to others, that it was actually isolated.

The discovery has been variously attributed to Brandt, Krafft, Kunkel, and Boyle. It would appear that either Brandt or Krafft was the original discoverer, but there is little doubt that Robert Boyle discovered it independently, for Kunkel himself stated that such was the case (see Kunkel's "Laboratium Chymicum," page 660, and Weigleb's "Geschichte des Wachsthums und der Erfindungen in der Chemie," v. i., p. 41). A paper deposited by Boyle with the secretaries of the Royal Society on October 10, 1680, and opened after his death, shows that he really obtained phosphorus from urine while the German process was still a secret (*Phil. Trans.*, 1692, v. 17, No. 196, p. 583).

Godfrey Hanckewitz, Boyle's assistant, appears to have been most expert in the manufacture, and is said by Thomson ("System of Chemistry," 1817, v. i., page 258) to have supplied all Europe for many years. According to Thomson, this phosphorus was known as "English phosphorus," but Hellot, who published the first complete description of the preparation, says that phosphorus was known throughout Germany as "Kunkel's phosphorus" (see "Mémoires de Mathématique, etc., de l'Académie Royale des Sciences," 1737, pp. 342 to 378). Hanckewitz gives a somewhat different version of the discovery of phosphorus, which will be found in the later portion of this article.

Probably the most reliable account of the discovery is that of Godfrey de Leibnitz in the "Miscellanea Berolinensia" (1710, v. i., p. 91 to 98). According to this account, "Brandt had fallen on a chymical process extant in a printed book, which taught how to prepare from urine a liquor fit to ripen a particle of silver into gold; and in laboring on this he found out his phosphorus. He had some acquaintance with Daniel Krafft, of the Council of Commerce to the Elector of Saxony; and, by his means, with Kunkel, one of the said prince's bedchamber, but who, under that character, performed chymical processes. On persuading Brandt that this arcanum might be sold to the great at a high price, and offering him their assistance, they obtained the composition from him. And upon going from Dresden to Hamburgh, they both saw and learned from him the process of the phosphorus. But Kunkel upon his return home had committed some mistake in the process, and for a long time could not hit upon the phosphorus, and he sent a letter to Brandt, complaining that the secret had not been sincerely communicated to him. But Brandt, repenting that he had been so easy in imparting the secret, delayed to satisfy him. Kunkel, in the meantime, after various trials corrected the error himself, whence he pretended to be the inventor, and of this Brandt bitterly complained.

"Krafft, who was a man of good address, undertook to vend the discovery among the great; and, in his way to England, he made a visit at Hanover, and ingenuously mentioned to me both the matter of the process and its author, Brandt; and he likewise showed the experiment of the phosphorus, to the great surprise of Duke John Frederic, and afterwards in England to King Charles II., Prince Rupert, the illustrious Mr. Boyle, and others, of which there is an account by Mr. Hooke. But he never, so far as I know, mentioned himself as the inventor. The phosphorus was first sent into France by me to Huygens, and at length the composition itself was by the illustrious Tschirnhausen, upon his return from Germany into France, communicated from me to the Royal Academy, to whom Huygens had already shown the thing. That Boyle had got but an imperfect description of it appears from his dissertation on phosphorus; for his phosphorus differs from Brandt's only in this, that it is more imperfect.

"But Duke John Frederic, as he was a magnificent and generous prince, ordered that I should send for the inventor. Brandt, therefore, came to Hanover and faithfully communicated to us the process, for whatever he did I imitated in another laboratory. Upon collecting a large quantity of urine, Brandt came to us, and went through the process. Upon Brandt's return to Hamburgh the duke settled an annual pension upon him, which was punctually paid him till the duke's death; and this probably was the only considerable encouragement which he reaped from his phosphorus."

Dr. Kunkel's phosphorus or "noctiluca" was also described in the "Philosophical Collections of Mr. Robert Hooke" (1681, No. 2, p. 8) by Dr. Sturm, who stated that Kunkel could extract phosphorus "out of any kind of terrestrial body whatever, as if it were there naturally placed."

Owing to the singular properties possessed by phosphorus, it occupied the attention of all the principal chemists whose writings are extant in the scientific literature of the period. Among these may be mentioned Tschirnhausen ("Anciens Memoires de l'Académie Royale de Paris," 1682, vol. i., p. 342), Homberg (*loc. cit.*, 1692, vol. ii., p. 135), Hofmann ("In Observationibus," Hall's edition, 1722, p. 336), Theichmeier ("Elementa Philosophiæ Naturalis et Experimentalis," 1724, p. 43), Nieuwentuit ("Existence de Dieu Demontree, etc.," p. 324), who obtained phosphorus from "old urine," which he collected from a hospital; Marggraf who gave in the "Miscellanea Berolinensia" (1743, v. vii., pp. 324 to 344) a plate of figures showing the furnaces which he employed, and others whose work is referred to later.

According to Chambers' "Encyclopædia" (1738), a Mr. Elzholt published in 1676 a special treatise dealing with phosphorus, and the "Aerial Noctiluca" of Boyle (1680), bearing on the subject, is well known.

The process employed by all the earlier investigators consisted in evaporating urine (which contains about 0.032 per cent. of phosphorus) to dryness and distilling the residue until the phosphorus passed over, and, considering that the chemists of the period adopted the process of destructive distillation as the best means of ascertaining the composition of nearly all organic bodies, it is remarkable that the discovery was not sooner made. The most successful workers appear to have been those who were most experienced in the use of furnaces, but some of them laid great stress upon the source of the urine, and that of beer-drinkers appears to have been in especial favor. Boerhaave ("A new Method of Chemistry." Translated by Shaw and Chambers, 1727, p. 196), however, says that the best is that from persons not much accustomed to drink wine.

Homberg mixed the dried urine with red bole, Boyle employed white sand, and Boerhaave powdered charcoal, but a very considerable improvement was introduced by Marggraf, who added lead chloride to the dried urine, and by Giobert, who first precipitated the phosphoric acid with lead nitrate and distilled the lead phosphate so obtained with charcoal ("Annales de Chimie," v. 12, p. 15).

The ignorance which prevailed among chemists as to the true nature of phosphorus is well shown in the following account from James' "Medical Dictionary" of 1745:

"Dr. Wall informs us that Mr. Boyle, being concerned to find how small a proportion of phosphorus was afforded by urine, desired him to look out for another subject that might afford it in greater plenty. The doctor afterwards causing a piece of dry matter to be dug up in the fields where night-men emptied their carts, he observed a great number of small par-