THE FIXATION OF ATMOSPHERIC NITROGEN.

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INTRODUCTION.

The great industrial problem indicated in the title of this article has been before chemists for half a century. It is doubtful whether there has been any real progress towards its solution since the ending of the first attempts to manufacture cyanides commercially and economically made by Possoz and Boissiere, at Newcastle-upon-Tyne, in 1844-1847. It would seem that the development of chemical theory within the same period should have thrown some light upon the more obscure points of the process, and the author has attempted in the following pages to define the present aspect of the problem, theoretically as well as practically. That the treatment is inadequate to the greatness of the subject he is fully aware. The limitations of his own time have made a fuller inquiry impossible at present. He can only hope that others may be led to follow up the subject more thoroughly. There is room for further experiment in this direction, both in the laboratory and on a large scale. The fixation of atmospheric nitrogen is an industrial problem to be compared with that involved in the manufacture of ammonia soda or of water gas, each of which passed through quite as discouraging an experience before attaining success as has, so far, been the lot of the nitrogen question. The question is still an open one, inviting further investigation. It has been taken up anew in recent years by Berthelot, from the theoretical side, and by Weldon from the industrial or practical side, and there is nothing in theory or practice at present to warrant the assumption that it is a hopeless question; in commercial importance it outranks either of the processes mentioned.

The matter given herewith relates principally to the preparation of cyanogen. The question of the synthesis of ammonia has been put somewhat in the background for lack of time and space. It is evident, however, that the fixation of atmospheric nitrogen in any one form is the solution of the general problem.

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* The substance of this article was prepared as an appendix to a commercial report, but has not been printed heretofore in any scientific journal.—A. A. B.

PART I.

HISTORICAL SUMMARY.

SHOWING THE PROGRESS AND DEVELOPMENT OF PROCESSES FOR THE MANUFACTURE OF CYANOGEN AND ITS DERIVATIVES.

Prussian Blue.

The familiar coloring matter, prussian blue, was discovered about 1710, but the chemical substance cyanogen, the radical common to prussian blue and to a large series of complex substances now known to chemistry, was not isolated until more than a hundred years later. The name cyanogen (generator of blue) was given by Gay Lussac, in 1814, to the new substance which he found to be the characteristic ingredient of this blue and of compounds related to it. The familiar name of "Prussiates," still applied in trade to the double cyanides of iron and potassium as well as the common name "Prussic Acid," by which hydrocyanic acid is known, bear evidence of the importance which the blue color originating in Prussia had early acquired as a commercial product.

Some time before the year 1710[1] a German manufacturer named Diesbach, working with the so-called Dippel's animal oil (commonly obtained by destructive distillation of bones, blood or other animal waste) happened, in handling a sample of this oil made from blood, to add to it a solution of potash (crude potassium carbonate) and obtained thereby a blue color. The process was soon applied upon a commercial scale. It was first described in a book called *Miscellanea Berolinensia,* published in 1710. But the discoverer of the color was not known by name until mentioned by Scheele in 1731.

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[1] **Richardson—Watt's Chemical Technology, Vol. I., p. 1, *et seq.* (Referred to hereafter as R.W.)**

Woodward & Brown, English chemists, each published a paper in 1724 upon the new blue. Woodward refers to a German from whom he had received directions for preparation of the blue, but gives no name.[1]

The process, as reported by Woodward, consisted in deflagrating a mixture of saltpetre and argols (crude potassium bitartrate) and fusing the product with dried blood. The resulting mass was lixiviated with water and the solution was treated with copperas and alum, producing a greenish precipitate which on heating with hydrochloric acid, yielded the blue color which has since been known as Prussian or Berlin blue. Brown (loc. cit.) substituted animal flesh for blood in the process. He also suggested that iron was essential to the color of the new substance.

Geoffry, in 1725, proposed the use of wool and charred horn instead of blood or flesh.

Scheele in 1731 published the name of Diesbach as the original discoverer. (R. W., loc. cit.)

In later modifications the use of nitre was abandoned and scrap iron was added to the mixture. The process as thus originated, is, in its essential features, that which exists to-day for the manufacture of potassium ferrocyanide from which prussian blue is made by precipitation with a ferric solution.

Potassium Ferrocyanide.

Macquer (1750–60 ?) first made ordinary yellow prussiate of potash (potassium ferrocyanide) in the crystalline form by treating prussian blue with a concentrated solution of caustic potash.

Beaumé in 1773 proved the presence of iron in the same salt. The fact that iron was an essential ingredient of the salt remained for a long time unknown ; as the proportion of iron varied in blue from different sources it was regarded as an impurity and many attempts were made to prepare a blue free from iron. Berthollet (1800-1806) determined the iron quantitatively.

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[1] Phil. Trans., 1724. 33-34, 15-25 In the original edition of the Transactions, Woodward's article is in Latin and the name of Diesbach is not mentioned. In the later, uniform edition the article is in English and the name of Diesbach is given, in a foot note, as the German referred to.—B.

The researches of Gay Lussac, in 1814, first placed the composition of prussian blue and its related substances upon an intelligible basis by showing that they all contain the radical cyanogen, a compound of carbon and nitrogen (CN) which combines with hydrogen to form an acid and with metals to form simpler or complex cyanides of which latter prussian blue, ferric ferrocyanide, $(Fe_7\ (CN)_{18})$ is a good example.

This knowledge at once led to inquiries into the chemistry of the commercial manufacture of yellow prussiate of potash, a process which had previously been purely empirical.

The researches of Liebig led to the general theory at present accepted, namely, that potassium cyanide is the first product of the fusion of nitrogenous animal matters with potash and that the yellow prussiate found in the liquor after leaching the fused mass results from decomposition occurring between potassium cyanide and a compound of iron, generally ferrous sulphide, which is formed in the fused mass by action of metallic iron upon the sulphur of the animal matters. In proof of this view potassium cyanide can be extracted by alcohol from the fused mass previous to the addition of water.

Muspratt, in 1820 (loc. cit.) obtained by direct lixiviation of the fused mass, crystallized yellow prussiate which had been obtained previously, by the method of Macquer, from prussian blue.

Mackintosh in 1824 used closed pots for fusion and applied mechanical stirrers.

Gautier[1] suggested in 1827 and Gentele[2] in 1835 practically applied the use of raw animal matter instead of charring it before fusion with potash as had been done previously.

Naumann in 1837 allowed the flame to play directly upon the fused materials.

Up to this time the large loss of nitrogen during fusion and the small yield of ferrocyanide with respect to the theoretical yield (never more than one-third, generally much less) seems to have attracted comparatively little attention. But the increasing de-

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[1] J. de Pharm, 1827, 11.

[2] Dingl. pol. J. **129**, 362.

mand for the prussiates in dyeing and the relatively greater cost of animal waste drew attention to the chemical problem involved in preventing this escape of nitrogen. It was found that the nitrogen was volatilized largely during fusion, as ammonia or organic bases, and the collection and utilization of these was attempted.

Kuhlmann in 1838[1] discovered that when ammonia was passed over red hot charcoal, cyanogen and ammonium cyanide were formed and by using a mixture of charcoal and potash for absorption he obtained potassium cyanide.

The idea of obtaining cyanides by passing ammonia over hot carbon, however, was probably of earlier origin.

Jaquemyn, applying this idea, passed the vapors from the prussiate pots over hot charcoal to obtain cyanides, and Berry[2] patented the same principle.

These facts relating to the conversion of ammonia into cyanides by the action of hot carbon are of interest as showing the development of chemical ideas upon the subject of cyanogen. They had their origin, however, mainly in the practical experience of the prussiate manufacture with its waste of nitrogenous vapors. Whatever interest they may have in connection with the history of the subject, they probably would not have led to the idea of atmospheric nitrogen as a source of cyanogen, except for another discovery originating also in an industrial process.

Cyanogen from Atmospheric Nitrogen.

Zinken in 1813[3] had found a mass of fused salt mixed with carbonaceous matter in the lower part of a furnace at Rothehüte, which he partly examined and supposed to be principally chlorides. Koch (*loc. cit.*) found a similar mass at Konigshüte in 1819. Berthier[4] also in 1826 remarked the presence of potassium carbonate as fused salt in the lower part of an iron furnace. No one seems to have tested these deposits or exudations for cyanogen until Dawes in 1835 announced the existence of potassium cyanide in them. No quantitative determination was made.

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[1] J. pr. Ch., **26**, 410.

[2] Eng. Pat., Jan. 21, 1840. Jsb. chem. Tech., 1858, 184.

[3] J. pr. Ch., **25**, 246. [4] Jsb. chem. Tech., 1879, 28.

In 1837 Neilson first introduced the use of the hot blast at the Clyde iron furnaces. Shortly afterwards,[1] a peculiar exudation of fused salt which hardened on reaching the air to a white, opaque mass was noticed upon the walls of the furnace near the boshes. The substance was regarded with much curiosity and it is related by Clark, who made the first analysis of the product, that its alkaline character was soon discovered by the workman and that it was used by the wife of one of them, for a time, as a substitute for soap in washing clothes.[2]

Clark's analysis showed it to contain potassium cyanide 43.4%, potassium carbonate 45.8%. No ferrocyanide was present. The mixture gave no blue color on addition of hydrochloric acid, but yielded a blue precipitate when ferrous sulphate (Copperas) was added previous to the addition of the acid in excess. This furnace went on producing potassium cyanide for three years from this time.

Zinken and Bromeis[3] found in the bottom of a hot blast charcoal furnace at Madgdesprung in the Harz a carbonaceous mass containing iron and lead and a saline matter, which, on lixiviation, yielded the following potassium salts, namely, ferrocyanide, cyanide, carbonate, silicate and manganate. A similar substance was noticed by Redtenbacher (R. W., *loc. cit.*) in a hot blast furnace at Mariazoll in Styria. Potassium cyanide was produced so abundantly in this case that it was sold commercially for galvanic gilding. The substance was found at the light hole, where the gases issue, and also in the pipes through which the gases pass from the furnace to the stoves.[4]

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[1] Probably produced more copiously in consequence of the action of the hot blast, as the circumstance had been only once reported before and has since been a common phenomenon of hot blast furnaces. Neilson had used the hot blast in iron furnaces as early as 1828, however. See "Bauerman's Metallurgy of Iron," p. 175.—B.

[2] Pogg. Ann., **40**, 315 ; Dingl. pol. J., **65**, 466.

[3] J. Pr. Ch., **25**, 246.

[4] I have, in my own experience, seen two cases of cyanide produced in blast furnaces. One from an anthracite furnace as an exudation from the wall below the boshes, the other from a furnace (at Irondale, West Va.), using coke, both, of course, hot blast furnaces. In the latter case no cyanides appeared upon the wall of the furnace, but a heavy, stony, grayish deposit formed in the downcast pipe through which the gases passed to the stove. It accumulated rapidly, forming a deposit like limestone in appearance, which threatened to clog the pipe and had to be broken away from time to time. Both samples were examined qualitatively, and found to be rich in cyanides. The gray color of the second sample was

Bunsen and Playfair[1] made an elaborate investigation of a furnace at Alfreton which yielded cyanides. The production of the substance was so abundant that it was estimated to amount to 224.7 lbs. in twenty-four hours. A hole was made in the front wall of the furnace, two feet nine inches above the tuyere or blast pipe, and the gases from that point were drawn off through a pipe for examination. Fumes of potassium cyanide escaped with the gases and condensed in the tube. Cyanides were obtained only from the lower part of the furnace; above the boshes none were found. These chemists believed that cyanides were produced only at a temperature corresponding to that at which potassium oxide gives up its oxygen to carbon. In the higher parts of the furnace cyanogen acts as a reducing agent and is destroyed by oxygen from the ores. When cyanides fall as low as the tuyere, on the other hand, they are burned, according to these authorities, by the blast of air. The conditions necessary for their production, therefore, are a reducing (deoxidizing) atmosphere or presence of hot carbon, and a temperature of the degree above mentioned.

Gases drawn from the furnace, as described above, had the following composition: Nitrogen 58.05%, Carbonic oxide 37.43%, Hydrogen 3.18%, Cyanogen 1.34%. These figures correspond to Nitrogen 79.2%, Oxygen 22.8% (instead of 20.08%; oxygen corresponding to water found in the gases is deducted). There is evidently here a deficiency of nitrogen as compared with ordinary air. At two feet above the tuyere no oxygen nor carbonic acid was found in the gases.

R. F. Smith[2] in 1865 found a compound oozing from the crevices of an old blast furnace at Kilmarnoch, which on analysis yielded 21.45% potassium cyanate, 47.73% potassium cyanide, 10.13% potassium carbonate.

A. v Kirpely[3] describes the escape of a quantity of fused salts, chlorides and cyanides, from the slag hole of the blast furnace of Alsó Sajó in Hungary, just before the escape of the slag.

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probably, due to coke dust. The mass was probably formed from spray or vapor of fused potassium cyanide which, passing out of the furnace, condensed and solidified upon the wall of the pipe where it first became chilled, binding together, as it hardened, the furnace dust which accompanied it.—B.

[1] Report of British Association, 1845.

[2] Jsb. chem. Tech., 1879, 44.

[3] Chem. News, 1865, Jsb. chem. Tech., 11, 54.

The facts just given had an important influence upon chemical thought. The source of the large quantities of nitrogen combined in the cyanides thus obtained became a subject of active discussion. It was not at once admitted that the free nitrogen of the air could be taken into combination with carbon to form cyanogen under the conditions existing in the blast furnace. The tendency was, at first, rather to find the source of nitrogen in the fuel or in the ammonia of the air. But the answer was given in a series af accurate experiments which left no room for doubt, and the direct fixation of atmospheric nitrogen by hot carbon under given conditions has long been accepted as a fact in chemistry.[1]

The paper of Bunsen and Playfair was read before the British Association in 1845, but to take up the discussion methodically we must go back a few years. As has been said, the production of cyanides in the blast furnace at once raised the question of the source of the combined nitrogen, and the problem suggested by the furnace was soon transferred to the chemical laboratory.

Lewis Thomson, of Newcastle-upon-Tyne, in 1839[2] first proved that potassium cyanide is produced when coke, potash and iron filings are heated to a high red heat in contact with air, and he received the medal of the Society of Arts for his discovery. Priority is claimed for Defosses, who made a similar discovery about the same time at Besancon in France.

Fownes and Young[3] also confirmed these statements in 1841, using carbon prepared from cane sugar and pure potash.

Erdmann & Marchand, however, in 1842[4] repeated Fownes' experiments and reported that the process was uncertain and required very exact regulation of conditions to produce any cyanides at all. They concluded that no cyanogen is produced when the materials are perfectly dry.

Berzelius[5] remarked that these results of E. & M. agreed with the earlier results of Wöhler, in that water was shown to be necessary

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[1] The experiments of Bunsen and Playfair showed also that, on the small scale and with a very slow current of nitrogen, *all* of the nitrogen was absorbed by the hot mixture of potash and carbon. It is much to be regretted that no record of the composition of the escaping gases was made in the commercial manufacture of cyanides by Possoz & Boissiere.—B.

[2] Dingl. pol. J. 73, 281.

[3] J. pr. Ch., **26**, 407.

[4] J. pr. Ch., **26**, 412.

[5] Jsb. d. fortschr. d. Chem., 1844, 23.

to the reaction. It was suggested that water plays the part of an intermediary in the reaction, first forming ammonia which is then converted into cyanide.

Langlois[1] discussed the question raised by Erdmann and Marchand. He made two experiments. 1. Moist, purified air was passed over a mixture of pure carbon and potash heated to high redness. Cyanogen was obtained. 2. Dry air under the same conditions also yielded cyanogen. The production of cyanogen in each case was tested by converting it into prussian blue in the solution obtained from the fused mass of carbon and potash. He found, however, that if a lead-glazed earthen tube were used instead of a porcelain tube, no cyanogen was obtained—lead in the glaze apparently docomposing cyanogen—and he ascribes the errors of Erdmann and Marchand to this fact.

Bunsen and Playfair[2] also attacked this question in their investigation above quoted. They passed nitrogen over a mixture of pure carbon and potash heated to high redness in a tube and obtained potassium cyanide. As the nitrogen was free from ammonia and the materials were chemically pure the origin of the nitrogen in the cyanide was placed beyond doubt.

Rieken[3] by very careful experiments confirmed the conclusion of Bunsen and Playfair as to the formation of cyanogen from pure carbon and nitrogen at a high temperature. He obtained pure carbon by heating pure cane sugar and pure potash by igniting pure crystallized potassium bicarbonate. The mixture of carbon and potash was then put into a tube and heated to whiteness, and nitrogen, prepared from air, was passed over it. This nitrogen was prepared by passing air through strong sulphuric acid and then through calcium chloride—thus removing both ammonia and water—then over iron filings heated white hot in a gunbarrel and finally through the mixture of white hot potash and charcoal. The highest white heat was required and the previous heating of the nitrogen was found to be essential. When the temperature was below whiteness no trace of potassium cyanide was formed.

Delbruch[4] added further to the weight of evidence in favor of

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[1] Ann. ch. phys. [3] **1**, 117.

[2] B. A. Rep., 1845.

[3] Dingl. pol. J., **121**, 286.

[4] Jsb. Chem., **1**, 473.

the conclusion of Bunsen and Playfair. He showed that the direct union of carbon and nitrogen was incontestable and extended the limits of existing knowledge upon the subject by describing other related reactions in which cyanogen is formed. Nitric oxide and "potassium carbonic oxide"[1] were shown to produce cyanogen when heated. Carbon dioxide (CO_2) mixed with ammonia, or even with nitrogen, when passed over hot metallic potassium, or ammonium carbonate kept in contact with fused potassium, also yielded cyanogen.

The fact of the direct union of nitrogen and carbon being settled and the practicability of carrying out the reaction on a commercial scale having been, in a certain sense, proven by the accidental phenomena of the blast furnace, attempts were made to build up a new manufacture, in which cyanides should be made direct from the nitrogen of the air.

The first patent taken out in England for manufacture of cyanides on the new principle was by A. V. Newton[2]. A patent taken out in 1839 by John Swindells[3] for the manufacture of cyanide might have come partly under the same head, as it involved the fusion of potassium or sodium sulphate, coal and iron in a reverberatory furnace. A portion of the nitrogen of the fire gases might have been taken into combination under these conditions as an alkaline carbonate is formed, but the process avowedly looked only to fixing the nitrogen of the coal as cyanide.

The specification of Newton especially prescribes that nitrogen from any source, but free from "oxidating substances" be forced through a layer of small pieces of charcoal saturated with "potashes" and heated to redness, the vapors containing cyanides to be absorbed by suitable liquids. He states that oxygen decomposes the cyanides at high temperatures; the necessity of excluding oxygen has always been recognized by other writers upon the subject as an essential feature of the process.

Newton used either charcoal, coal or coke, but preferred the former, in pieces the size of a hazelnut. The charcoal was satu-

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[1] The compound of the potassium retort (?)—B.

[2] Dingl. pol. J., 95, 293. Eng. Pat. No. 9985, Dec. 13, 1843.

[3] Eng. Pat. No. 8086.

rated with a strong solution of potash and dried before being put into the retort. A definite, maximum proportion of alkali was used; an excess prevents complete absorption of nitrogen and a deficiency involves loss (of carbon?). Twenty-five to one hundred parts of potash are used to one hundred of coal, according to the density of the latter. Nitrogen should always be in excess, but must not be passed too rapidly. A certain pressure upon the gas and much friction with the solids through which it passes are favoring conditions.

Newton recommends the use of waste gases from the sulphuric acid chambers after passing through ferrous sulphate and lime-water, to remove oxides of nitrogen. The use of these chamber gases has also been suggested by Binks, Firman and others.[1]

Before the date of Newton's patent, however, Possoz and Boissiere[2] had been at work upon the same industrial problem in France and had in operation at Grenelle, near Paris, in 1843, a small plant which was turning out yellow prussiate at the rate of 15,000 kilos, or more than fifteen tons per annum. The high price of fuel and the need of a cheap and abundant supply of highly refractory clay for making the retorts used in the process led them to remove, in 1844, to Newcastle-upon-Tyne, England, where they went into the operation on a large scale, under the patronage and coöperation of Bramwell and Hughes. The works here, in 1845, turned out yellow prussiate at the rate of more than a ton a day. They were run until 1847, and were then abandoned after considerable loss. The salt was said to be produced at the rate of less than two francs per kilo, and was of exceptionally fine quality.

This is the most persistent attempt on record to establish commercially a process for the fixation of atmospheric nitrogen, and as such deserves close consideration.

The process consisted of passing the gas from a coal fire through large vertical cylinders or retorts of fire clay filled with a mixture of wood charcoal and potash. The charcoal was prepared by saturating it with a solution of potash and then drying. Much

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[1] R. W., Vol. I. Pt. V. 61-65.

[2] Jeb. chem. Tech., 1855, 83; 1858, 191. Dingl. pol. J., **104**, 446; **107**, 444; **129**, 361; **149**, 56.

stress was laid by P. and B. upon exclusion of water in the process. The retorts were kept at the highest possible temperature—a white heat being preferred—as the rate of conversion of potash into cyanide was found to be proportional to temperature. The conversion was commonly completed after ten hours, but 2—3 hours in some cases was sufficient, with a good white heat. The cyanized charcoal was withdrawn at the bottom of the cylinder and dropped into a tank of water containing powdered spathic iron ore in suspension, by which the cyanides were converted into ferrocyanides or prussiates. The solution was finally filtered and evaporated to crystallization. The apparatus worked continuously[1].

In the French experiments the retorts were seven to eight feet long with walls 2—3 inches thick. In England, much larger and heavier retorts were used. The high temperature, in connection with the alkalies, caused rapid destruction to the retorts. They were heated white hot before the introduction of the alkalized coal. White hot flues also served to superheat the nitrogen or furnace gases before entering the retorts. In later forms of the apparatus air was admitted directly to the cylinders, oxygen being removed in passing through the upper layers of carbon. The presence of carbonic oxide or carbon dioxide, as in the fire gases, was found to be disadvantageous. Coke yielded less cyanogen than charcoal. The production of cyanide was said to be greater for a given weight of potash than by the old prussiate process. The alkalized charcoal contained 30% of potash. Soda was found inferior to potash and required a higher temperature. Water, even in small quantities, hindered the production of cyanogen. This fact was ascribed by P. and B. to decomposition of the latter by water to form ammonia.

In the latest constructions the cylinders were 10 feet in length and 2 feet in diameter with walls 9 inches in thickness. These were built of fire brick and their massive character enabled them to retain heat and to resist wear so as to last several months in use. Lateral slits were also made in the walls of the cylinders for admission of air direct, and through these slits the contents could be

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[1] A cut of P. & B.'s furnace is given in R. W; p. 63.

stirred to prevent clogging by fused potash which had been one of the chief obstacles in the process. The current of gas was upward and the charcoal was fed in at the top in moist condition and dried thus by waste heat. A pump drew the gasses through the cylinders.

The causes of failure assigned in England were the rapid destruction of apparatus owing to corrosion of the retorts by the alkali, and the great loss of alkili by volatization, or absorption by the cylinders. Much potash was wasted in the fine charcoal after lixiviation or converted into silicates and other salts useless for further application in the process. Bramwell[1] patented some of the later improvements of P. & B.'s plant which were devised by him (Eng. Pat., Oct. 8, 1846). He preferred to convert oxygen of the air into carbonic acid rather than carbonic oxide before carrying it into the cylinders. The use of lateral slits is also a feature of his patents.

This process is said also to have been applied at several places in France, but was ultimately abandoned.

R. Laming, in 1843,[2] patented a process for manufacture of hydrocyanic acid by passing ammonia through red hot charcoal.

Swindell, in 1844,[3] patented a process in which nitrogen or air or oxides of nitrogen were passed through charcoal or other carbonaceous material, heated to full redness in a perfectly close retort. If ammonia is to be formed, steam is mixed with the nitrogenous gas.

J. Laming obtained a patent in 1845,[4] (for another party), by which charcoal or other form of carbon in powder is mixed with alkali and the mixture is kept in fusion while a current of ammonia is passed through it for the production of cyanides.

Bunsen[5] proposed the construction of a furnace for the production of cyanides on the plan of the blast furnace. It was to be charged with alternate layers of coal and alkali and the fused cyanide was to be drawn off periodically at the bottom (p. 8). No industrial application of this idea is known, although Binks is

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[1] Dingl. pol. J., **104**, 446.

[2] Eng. Pat., No. 9832, July 13, 1843.

[3] Eng. Pat., June 12, 1844.

[4] Eng. Pat., No. 10955, Nov. 18, 1845.

[5] Rep. Brit. Assoc., 1845.

said (R. W., p. 66), to have taken out a patent for a similar furnace.

Armengaud patented in France, in 1846, a furnace for manufacture of cyanides from the nitrogen of the air.[1] Unlike P. & B. he regards the presence of steam as favorable to the process and prescribes its regular admission to the furnace. The charcoal, which must be in excess, is intimately mixed with potash, soda or lime, the mass is heated to a cherry red and over it is passed a mixture of furnace gases and steam. The absorption chamber resembles a reverberatory furnace. The product is leached with water at 75–85°C. The volatile products from the furnace are carried into a solution of ferrous sulphate.

F. Ertel in 1846 took out a French patent for a process very similar in principle to the above,[2] involving the use of steam, or better as the inventor says, of hydrogen. Air from a coal fire is passed through a column of coal or coke heated to a cherry red and from this through a mixture of charcoal powder and alkaline carbonates or lime, also heated to cherry red. The distinctive features of Armengaud's and Ertel's process are the use of steam and the application of a comparatively low temperature, whereas Possoz and Boissiere insisted upon a white heat and the exclusion of steam, as essential conditions.

The history of later attempts to utilize the nitrogen of the air for the manufacture of cyanides, shows, up to the present time, no commercial success. The few further plans or suggestions bearing upon the question are added here as having a possible bearing upon the future study of it.

Margueritte and Sourdeval in 1862[3] found that when air is passed over a hot mixture of baryta and carbon, nitrogen is absorbed freely, forming barium cyanide, and that this compound in presence of steam at 300°C. yields ammonia. In another form of the process they passed a mixture of illuminating gas and nitrogen over a mixture of coal and barium carbonate. The resulting barium cyanide was decomposed in solution by potassium sulphate.

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[1] Dingl. pol. J., **120**, 111 (with diagram); Genie Industriel, 1853, 315.

[2] Dingl. pol. J., **120**, 77; French Pat., Nov, 16, 1846.

[3] Jsb., chem. Tech., 1873, 361; Ber. 1878, 79.

They also used iron filings in one of their methods similar in other respects to the foregoing. This process, which seemed to promise much for the industrial uses of nitrogen, has never received any commercial application, even as a source of ammonia[1]. English patents for the process were taken out by Clark.

Diess in 1873[2] patented in France a method for the manufacture of cyanides which differs in no essential feature from that of Possoz and Boissiere (p. 12).

S. Q. *and A. Brin, in 1883,*[3] *patented a process for manufacture* of ammonia by passing moist nitrogen over coke containing baryta, which recalls that of M. and S. They also utilized oxygen separated from the air by another process.

Berthelot,[4] in 1868, made a valuable contribution to the theory of the synthesis of cyanogen. He obtains acetylene ($C_2 H_2$) by direct combination of its elements (under the influence of the electric spark) and converts this in presence of nitrogen by the same means into hydrocyanic acid ($H C N$). He says that when nitrogen acts upon a highly heated mixture of nitrogen and potash, the compound potassium acetylene ($C_2 K_2$) is first formed and that this, by direct union with nitrogen, forms two molecules of potassium cyanide ($K C N$).

J. Blair,[5] in 1878, patented an apparatus in the United States for manufacture of cyanides. Gases from a coal fire (a stack with a deep layer of coal) are drawn over a layer of heated iron ore to form carbonic acid by oxidation of the carbonic oxide. The former is absorbed by passing the gases through milk of lime, and the resulting nitrogen is carried to a holder. The nitrogen is then carried upwards through a hot mixture of potash and charcoal in a stack heated externally by a fire in a larger stack which encloses it. The charcoal is drawn from the bottom and leached. Fumes of potassium cyanide which escape from the stack are condensed in a chamber adjoining and the lighter fumes are absorbed by a solution of a salt of iron.

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[1] Comptes Rend., **50**, 1100 ; Dingl. pol. J. **157**, 73, 357.

[2] E. Meyer, Jsb. chem. Tech., 1874—442.

[3] Eng. Pat. No. 5802, Dec. 18, 1883.

[4] *Jsb. chem. Tech., 1869, 260:* Comptes Rend., **67, 1141**; J. pr. Ch., **107,** 272.

[5] *Scientific American*, 1878, 21 (with cut), Dingl.; pol. J., **230,** 93.

Walter Weldon, in 1879,[1] obtained a patent in England for the manufacture of cyanides. He finds that the temperature necessary for absorption of nitrogen by alkaline charcoal is not so high as has been supposed.[2] Instead of a white heat, Weldon finds that a comparatively low temperature, a bright red or even a lower heat, suffices to produce cyanides from mixtures of alkalies or alkaline earths with carbon in presence of air. His apparatus consists of a rotary furnace similiar to that used in preparation of black ash (soda ash).

V. Alder, in 1881[3], brought forward a method involving some new features. Oxides, hydrates or carbonates of the alkalies or alkaline earths with charcoal are used to absorb nitrogen prepared by passing air or fire gases through solutions of potassium or barium sulphide or by passing air over iron, copper or zinc. He asserts that presence of finely divided metallic iron is useful in the process[4] and supplies this by saturating charcoal or coke with a solution of ferrous sul phate and then igniting it in a current of hydrogen. Sulphates and sulphides of the alkalies are also used, together with lime, in place of other alkaline bodies above mentioned. In a later patent (D. R. Pat., No. 18, 945, 1881) the admixture of hydrocarbon gases or carbonic oxide with the nitrogen is recommended; also the fuel in fragments is coated with a pasty mass made by mixing a strong solution of a soluble salt with charcoal powder, sawdust, etc. These modifications are introduced with the object of increasing the surface available for absorption of nitrogen.

Ludwig Mond, in 1882[5], obtained a patent for manufacture of cyanides and ammonia by calcining, out of contact with air, a mixture of carbon, barium carbonate, or oxide, and magnesia, previously

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[1] Jsb. chem. Tech., 1879, 472.

[2] Armengaud and Ertel (p. 20) both advocated the use of moderate temperatures—cherry red—and Margueritte and Sourdeval showed that baryta in presence of charcoal absorbed nitrogen at a comparatively low temperature, and that a light red or even a lower temperature is sufficient.

[3] Jsb. chem. Tech., 1881, D. R. Pat. 12,351. 1882, 509.

[4] This was suggested by L. Thomson in 1839. It would naturally occur to any one familiar with the old prussiate process, but the conditions are different in the two cases and the reason for using it here is not apparent. The carbide of iron may possibly play an intermediate part in the production of cyanogen, such as Berthelot supposes to be played by C_2K_2, as above quoted.—B.

[5] U. S. Pat. 269,309, Dec. 19, 1882.

compressed into blocks, and then exposing these heated blocks to a current of nitrogen. In an improvement he first heats the nitrogenous gas by passing it through hot barium salts and then passes it through fresh layers of barium salts and carbon at the temperature required for forming cyanogen compounds.

Fogarty, in 1883,[1] took out two patents in the United States for production of cyanides and ammonia, which consisted essentially in dropping a mixture of powdered carbon and alkali into superheated furnace gases or superheated "generator gas" (a mixture of nitrogen, hydrogen, carbon dioxide, carbon monoxide, and steam), whereby cyanides were produced, which were subsequently decomposed by steam, yielding ammonia. He also obtained two similar patents in 1887[2]. In one of these processes the mixture of superheated furnace gases or generator gas is mixed with steam in excess, with the object, as explained by the author, of first producing cyanides and cyanates, and then, in the same mixture, decomposing these by the steam present to produce ammonia.

In the second of these patents both air and steam are in excess. Cyanides are supposed to be produced, and subsequently decomposed by the excess of steam to produce ammonia. The latter in presence of carbonic acid of the mixed gases is supposed to form ammonium carbonate, and this is said to be decomposed by gypsum, yielding calcium carbonate and ammonium sulphate. These processes have been tried on a large scale experimentally, but are not as yet commercially successful.

J. Young, in 1884[3], patented a process for cyanides intended to meet the difficulty hitherto encountered in the rapid destruction of the apparatus. He proposed to use magnesian lime stone or other suitable basic substance for constructing the retorts.

Siepermann[4] (1887) obtains cyanates by passing ammonia over a mixture of barium carbonate with alkaline carbonates. For cyanides he adds coal powder to the mixture. He gives the results of experiments, showing the effect of temperature upon the production of cyanides. Excessively high temperatures yielded poorer results than a moderate red heat.

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[1] U. S. Pat. 288,323 and 402,324, Nov. 13, 1883.

[2] U. S. Pat. 371,186, and 371,187, Oct. 11, 1887.

[3] Jsb. chem. Tech., 1887, 675.

[4] Eng. Pat. No. 16046, Dec. 6, 1884.

Dickson in 1887,[1] patented a process for production of cyanides and ammonia by injection of a mixture of air, steam, coal dust or hydrocarbon vapor, and powder of alkalies or alkaline earths, into a chamber heated by the combustion of the injected, finely divided fuel alone. His method also contemplates the maintaining of pressure (one to three atmospheres) in the furnace.

The Formation of Metallic Nitrides.

R. Wagner in 1857[2] had suggested that nitrides of boron and silicon in the interior of the earth might be the source of the ammonia found in combination with boric acid in the lagoons of Tuscany and as sal ammonic in volcanic exhalations. This ammonia may be a product of the action of water at high temperatures upon the above nitrides. Bunsen, however, and Rainer, (*loc. cit.*) regard volcanic ammonia as of organic origin, resulting from action of subterranean heat upon fossil vegetable matter, coal, lignite, etc.

Brieglieb and Geuther in 1862[3] investigated the question of the metallic nitrides. The close relation of these bodies to the cyanides renders a knowledge of them of much interest in this connection. Nitrides of magnesium, aluminium and chromium were obtained by simply heating the metals in pure nitrogen. The temperature of combination of nitrogen with the metal seems to be near the melting point of the latter. Magnesium nitride is a greenish yellow, amorphous mass which yields ammonia in contact with water or caustic alkalies, and yields cyanogen when heated in an atmosphere of carbonic oxide, or carbon dioxide. It has the composition $Mg_3 N_2$.

Tessie de Motay in 1872[4] announced that titanium nitride could be made to yield ammonia by the action of steam and could then be regenerated by submitting it to a current of nitrogen and the action thus alternated successively.

Mallet in 1876[5] obtained magnesium nitride by the combustion of

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[1] U. S. Pat. No. 370,768, Oct. 4, 1887.

[2] Jsb. chem. Tech., 1857, 121.

[3] J. pr. Ch. 123. 228.

[4] Jsb. chem. Tech., 1873, 279; Ber., 1872, 395.

[5] Proc. Am. Chem. Soc., **1**, 17.

magnesium powder in a crucible with insufficient admission of air. Other nitrides, of boron, titanium, silicium, etc., have been investigated by Ufer, Uhrlaub, Wohler, Deville and Caron.[1]

Cyanogen from Oxides of Nitrogen.

Binks[2] proposed to use oxides of nitrogen or vapor of nitric acid for production of cyanides. The gases were brought in contact with vapors of hydrocarbons in passing through a highly heated cylinder filled with firebrick. When the nitrogen compounds are in excess ammonia is chiefly produced, but with hydrocarbons in excess cyanides are the principal products. Crane and Jullion (*loc. cit.*) used a somewhat similiar process, using, however, an excess of water gas (hydrogen and carbonic oxide) mixed with the oxides of nitrogen and hydrocarbon vapors, and passing the mixture over a hot catalytic substance (platinized asbestos) at a temperature of 600° F.

Firman (*loc. cit.*, p. 65) and others have proposed the use of waste gases of the sulphuric acid chamber (nitrogen, oxides of nitrogen, etc.) for the same purpose.

A process suggested by Roussin in 1858[3] uses oxides of nitrogen in a different way and recalls the very early methods of Diesbach and Woodward (p. 4). With the object of converting nitrates into cyanides he made the following experiment: Four equivalents of crude potassium acetate were mixed with three of potassium nitrate (nitre) and five of potassium hydrate or carbonate, and heated in a porcelain crucible to 350° C. The mass burned briskly leaving a black residue which, on lixiviation, yielded potassium cyanide and carbonate. By addition of coal powder, to make up for the deficiency of carbon in the organic acid, an increased yield of cyanide was obtained, but still short of the theoretical result. Previous reductions of the nitrate to nitrite yielded better results, and a mixture of potassium acetate and nitrite with lampblack gave 2.6 parts of Berlin blue (dried at 100° C.) to 13 parts of acetate, and an ammoniacal odor during the operation showed a loss of nitro-

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[1] J. pr. Ch., **101**, 359; **103**, 230: **105**, 69: **110**, 248.

[2] R. W., Vol. 1, Pt. V., p. 60. Eng. Pat. No. 10911. Nov. 3, 1845.

[3] Comptes Rend.. **67**, 875. J. pr. Ch., **78**, 375.

gen. Potassium tartrate yielded little cyanide when used to replace the acetate, a fact already announced by Guibourd. Roussin suggested that a commercial process could be based on the use of crude sodium nitrate and acetate.

Production of Cyanides from Ammonia.

The reactions by which ammonia is converted into cyanides are so closely related to the direct production of cyanides from nitrogen and offer so many points of suggestion in connection with the same, regarded as an industrial problem, that the history of them cannot be omitted from this summary.

The original experiment, ascribed by Langlois[1] to Scheele, of heating together sal ammoniac, potash and charcoal and obtaining potassium cyanide may be regarded as the starting point.

Liebig attributes to Scheele (1750–80 ?) the statement, that ammonia passed over hot charcoal yields hydrocyanic acid, but Langlois does not find this in Scheele's writings. What Scheele does say is that when sal ammoniac is heated with vegetable charcoal and potash the mass yielded on lixiviation "*la lessive du sang.*"[2] (Langlois, loc. cit.)

Clouet in 1791[3] mentioned that ammonia gas passed over hot charcoal yields hydrocyanic acid. He states that Thenard had noticed that a soluble substance having the odor of bitter almonds was formed under the same conditions. Bonjour, Vauquelin, Buchholz, Schroder and Ittner[4] all refer to the same fact as based upon experiments in which ammonia or ammonium chloride was heated with charcoal or with mixtures of charcoal and lime or oxide of lead.

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[1] Ann. ch. phys. [3] **1**, 117.

[2] That is, potassium ferrocyanide, yellow prussiate of potash, called also in German "blutlaugensalz." The iron must have come from impurities in the materials. In the "Life of Scheele," given in Crell's Journal, Vol. I, p. 12, 1891, the author says: "His experiments on the coloring matter of Prussian blue, the methods of separating it, its properties and in short the discovery of its artificial composition from charcoal, fixed alkali and sal ammoniac, may be mentioned amongst the most valuable of the performances with which he has presented us." The biographer also refers to fuller accounts of this work in The New Transactions of the Royal Stockholm Academy, Vol. III, p. 256, and Vol. IV, p. 32. These sources of information are not accessible to me.—B.

[3] Ann. ch. phys., **11**, 30; J. pr. Ch., **26**, 408. Crell's Annallen 1796. This latter reference, which is probably the original source, I have not had access to.—B.

[4] J. pr. Ch. **26**, 409.

The product was probably ammonium cyanide, as in later repetitions of similar experiments, but the constitution of the cyanides was not then understood as this was before the date of Gay Lussac's discovery (1814). Clouet reported that hydrocarbons, carbonic acid and nitrogen were set free at the same time, while Bonjour showed that hydrogen was the only by-product, an observation that was fully confirmed by Langlois in 1841. Trommsdorf,[1] however, was first to recognize ammonium cyanide in the products of this experiment.

Kuhlmann[2] found that volatile nitrogen compounds containing all hydrogen or mixed with volatile hydrocarbons, when passed together with carbonic oxide over hot platinum sponge, yielded ammonia. He refers to Clouet's experiment, and shows, by a repetition of the same, that no hydrocyanic acid, but only ammonium cyanide, is produced. Marsh gas (CH_4) is separated at the same time. He regards the process of preparing alkaline cyanides as involving first the formation of ammonia, which, in presence of alkali and excess of carbon, is converted into cyanogen and carbonic oxide. Langlois[3] repeated Scheele's experiment with sal ammoniac, but obtained no cyanide. He also obtained ammonium cyanide by passing ammonia over hot charcoal, and called attention to the remarkable way in which ammonium cyanide resists decomposition at high temperatures.

The processes of Jacquemyn and Berry in this direction have already been mentioned (p. 6).

Graeger[4] passed vapor of ammonium carbonate through alkaline charcoal contained in narrow iron cylinders 1½ inches in diameter, and obtained 93 to 95% of the theoretical yield of ferrocyanide. When large and wide cylinders were used the results were much inferior, only 15 to 30% being obtained.

Brunquill,[5] in 1856, proposed to apply the same principle to the production of cyanides and prussiates. Ammonia, or the vapors from distillation of bones, etc., are passed over hot firebrick

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[1] Ibid.

[2] Ibid. Ann. Chem. (Liebig), 38, 62 : J. pr. Ch., **16**, 482.

[3] Ann. ch. phys. [3], **1**, 117.

[4] Jsb. chem. Tech., 1858, 184.

[5] Preuss. Verhandlungen, 1856, 30. Jsb. chem. Tech., 1856, 102. Dingl. pol. J., **140**, 374, 452.

and then over hot wood charcoal in pieces of the size of a chestnut. The volatile ammonium cyanide is absorbed by solution of ferrous sulphate in an apparatus of peculiar construction. A portion of the ammonia is recovered as sulphate, and used anew in the process. The precipitated cyanides of iron are converted by potash or soda into prussiates. The advantages of this method are the prevention of waste of potash and of nitrogen. Only moderate temperatures being employed, there is no loss of potash by volatilization, by absorption, or by formation of unavailable salts of potash, all of which occur in the old process. The cost of the ammonia is defrayed by the increased value of the residue when bones are used. The author hoped also to obtain ammonia for the first stage of the process by passing air and steam over coal.

Levoir, in 1859,[1] noticed that a flame of ammoniacal gas yielded cyanogen (ammonium cyanide) in burning. Fischer[2] questioned this statement, saying that he had repeated Levoir's experiment with an argand burner, and obtained no cyanogen. The fact was verified, however, a few years later by Romily.

H. Johnson,[3] in 1860, obtained in England a patent for a method, devised by J. V. Lucas in Paris, for preparation of prussiates, which consists simply in saturating wood charcoal with potash solution, drying and heating it to redness in a retort, and passing ammonia over it. The charcoal is mixed also with 5% of iron filings.

J. Webster, in 1860,[4] patented in England a process for manufacture of prussiates by charring or burning a mixture of sawdust or spent bark and oxide of iron, charging the mixture with potash and passing ammonia through it.

Fleck,[5] in 1863, proposed to make cyanides as follows: A hot mixture of charcoal or coal, sulphur and potash is treated with a definite quantity of ammonium sulphate. Potassium sulphocyanate is formed. Ammonia in part escapes, but is absorbed and utilized. The sulphocyanate is decomposed by metallic iron, yielding

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[1] J. Pr. Ch., **76**, 447. Dingl. pol. J., **153**, 466.
[2] Dingl. pol. J., **157**, 466.
[3] Dingl. pol. J. **156**, 212. Jsb. chem. Tech., 1860, 221, (with diagram).
[4] Eng. Pat., No. 1913, Aug. 8, 1860.
[5] Polyt. Centralbl., 1863, 717. Dingl. pol. J. **169**, 209. Jsb. chem. Tech., 1863, 323.

potassium cyanide and ferrous sulphide. It was claimed by the author that 94.42% of the ammonium salts used were ultimately converted into cyanides. This process is referred to by Meyer ten years later, 1874, as not being successful in practice.

Gelis,[1] in 1862, manufactured prussiates in Paris after a new method of his own invention, for which a medal was awarded at the London Exhibition of 1862. It consists in mixing, in the cold, a solution of ammonium sulphhydrate ($N\ H_4\ H\ S$), obtained from gas liquor, with carbon disulphide: ammonium sulpho-carbonate $(NH_4)_2SCS_2$) is formed and sulphuretted hydrogen. The addition of potassium sulphide to the sulphocarbonate results in the production of potassium sulphocyanate, which by action of iron can be converted into cyanide or prussiate. The by-products, ammonium sulphate and sulphuretted hydrogen, are again used. The process is carried on in a retort and these products are readily recovered. The cost by this process was said by Payen to be within 1.6 francs per kilo (about 15 cts. per ℔.) for potassium ferrocyanide.

Meyer, in 1874 (p. 25), remarks that the conversion of potassium sulphocyanate into cyanide by iron is wasteful of nitrogen when fusion is resorted to and incomplete in the cold. The process of Gelis was finally abandoned.

Romily,[2] in 1867, repeated the experiment of Levoir (p. 27), and improved upon it. Illuminating gas was made to bubble through ammonia and then burned from a jet, and the flame was made to impinge upon a surface of water containing caustic potash in solution. Potassium cyanide was found after a time in the solution. Solutions of sodium and calcium hydrates gave corresponding results. When distilled water was used ammonium cyanide was found in the liquid. The effect was produced only when the flame was luminous or smoky; the flame of a Bunsen lamp yielded no cyanides. Vapors of oils or hydrocarbon gases containing ammonia gave similar results. Vapor of water in the mixture of gases did not prevent the formation of cyanides. When iron in fine powder

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[1] *Annales du Conservatoire des Arts et Metiers*, 1862, 37. Jsb. chem. Tech., 1862, 283.

[2] Compt. Rend. **64**, 320; **65**, 865. Jsb. chem. Tech., 1867, 761.

was suspended in the alkaline solution ferrocyanide was formed.[1]

An apparatus was devised to apply the principle industrially. A cylinder of iron revolving on a horizontal axis, dipped into a tank containing an alkaline solution. A pipe, parallel with the cylinder and pierced with holes, supplied ammoniacal illuminating gas, burning in a line of jets which impinged upon the face of the cylinder. The cyanides were absorbed by the film of alkaline liquid which was continually renewed as the cylinder revolved.

Schwarz,[2] in 1869, obtained ammonium cyanide by passing vapor of carbon disulphide mixed with ammonia over hot iron or copper in an iron tube. Sulphide of the metal is simultaneously formed. The vapors are passed into a mixture of solutions of caustic potash, ferrous sulphate and ferric chloride and the resulting mass is converted into Prussian blue by hydrochloric acid, and then by potash into yellow prussiate. Schwarz also confirmed the conclusions of Levoir and Romily (p. 23–24) as to the production of ammonium cyanide during the combustion of ammoniacal illuminating gas, and he suggests that the purification of such gas from ammonia is, on this account, a matter of the greatest importance.

Frohde remarks[3] that the fumes from burning coal may be noxious, not merely because of oxides of carbon in them, but also because of cyanogen. He claims to have detected cyanogen by its odor where coal was incompletely burned.

E. Meyer,[4] in 1874, published a review of the cyanogen industry up to the year of the Vienna Exhibition (1873). He found the old method still the only important one. The problem of making cyanides from nitrogen of the air was still unsolved, and the earlier efforts of Possoz and Boissiere (p. 12) had not been even equalled in its results by the later one of Margueritte and Sourdeval, from which much was at first expected. The methods using ammonia as a source of nitrogen for the manufacture of cyanides had not re-

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[1] The discoveries of Levoir and Romily recall the early observations of Kuhlmann, who showed that ammonia and all volatile compounds of nitrogen yielded ammonium cyanide when mixed with hydrocarbons (or even with carbonic oxide in the case of ammonia), and passed over platinum sponge at a temperature of 600° F.—B.

[2] Bull. soc. chim., 1869, 167. Dingl. pol. J., 191, 399. Jsb. chem. Tech., 1869, 269.

[3] Watt's Dict. Supp., I., 537.

[4] Jsb. chem. Tech., 1874, 442.

placed the old method, through dry distillation of animal matters, (Karmrodt, and others)—which are treated by fusion in the old process—nor by substitution of ammonia salts as a source of nitrogen for these substances (Fleck, p. 23). Neither had the methods based upon formation of sulphocyanate (Gelis) marked any great success. The production of sulphocyanate is readily brought about by Gelis' method and the process is, so far, a success; but the conversion of this salt into cyanide or ferrocyanide is difficult. It does not stand sufficiently above the usual raw materials (animal matters) used for this purpose, in its proportion of nitrogen, to counterbalance the disadvantage which it offers in comparison with them from its high proportion of sulphur.

F. Maxwell-Lyte[1] patented, in 1875, a process for manufacture of ammonia by bringing nitrogen in contact with nascent hydrogen liberated in the presence of a triad or pentad element.

Tscherniak and Gunsberg,[2] in 1878, patented a method, in Germany,[3] for the manufacture of cyanides similar in principle to that of Schwarz (p. 25). Two parts of ammonia water of 85%, and one of carbon disulphide are put into a tight vessel, heated to 110° C. below and cooled above so that a continuous distillation of the volatile substances occurs. After three or four hours the mixture is found to be converted into ammonium sulphocyanate and sulphuretted hydrogen. The ammonium salt is converted into calcium sulphocyanate, which, by action of an alkaline sulphate or carbonate, yields the corresponding alkaline salt, and this, by heating with coal, lime and iron, yields cyanides or prussiates. The ammonia is recovered and used again.

Graham Young, in a process for the manufacture of ammonia patented in England in 1880, has suggested the use of electricity to effect the union of nitrogen and hydrogen. The principle had also been mentioned in an English patent issued to Chisholm and Kent in 1860. No practical result has as yet come from these suggestions.

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[1] U. S. Pat. 161,137, March 23, 1875.

[2] Ber., 1879, 140. Dingl. pol. J., **232**, 80. Jsb. chem. Tech., 1879, 471; 1882, 570.

[3] D. R. Pat. 3,199. April 9, 1878.

The Decomposition of Alkaline Hydrates by Metals in Presence of Air to Produce Ammonia.

Dufrené[1], in 1880, patented a process in England for the manufacture of ammonia by combustion of zinc in air, in presence of an alkaline hydrate. Hydrogen and nitrogen are both set free and combine to form ammonia under the influence of a porous solid, such as iron or platinum sponge in a heated state.

Twinch[2], in 1881, proposed to manufacture ammonia by using oxide of nitrogen (nitric oxide ?—B.) to remove oxygen from air; the resulting nitrogen (which is said to be nascent and peculiarly active?—B.) is brought in contact with nascent hydrogen from the decomposition of steam or of alkaline hydrates by metals, to produce ammonia.

(*To be concluded.*)

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[4] Eng. Pat. No. 5478, Dec. 29th, 1880.

[1] Eng. Pat. No. 3712, Aug. 25th, 1881.