THE FIXATION OF ATMOSPHERIC NITROGEN.

BY

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(*Concluded.*)

PART II.

AN INQUIRY IN REGARD TO THE CONDITIONS UNDER WHICH CYANOGEN IS PRODUCED BY DIRECT UNION OF NITROGEN AND CARBON.

The union of nitrogen with other chemical substances is brought about with so much difficulty that it has long been the custom to speak of nitrogen as an inert substance showing little affinity for or tendency to combine with other elements, yet the very large classes of compounds in which nitrogen is an essential element show that it is not difficult to retain it in a compound once formed, or to hand it over from one compound to another in the reactions by which chemical compounds are formed or decomposed. The difficulty then, is simply that of getting free nitrogen, as it exists in he air, to enter into direct combination with any other element, and this difficuly is so real and serious that, practically, all of the nitrogenous compounds used in the arts are obtained by the decomposition of other nitrogen compounds. Free nitrogen is one of the most abundant substances on the earth, and combined nitrogen is essential to some of the most valuable of commercial products, but the ready fixation of the nitrogen of the air on a manufacturing scale in any single compound which may be used as the starting point of a series of substances derived from it, has yet to be accomplished.

This indifference to combination together with the considerable degree of permanence given by nitrogen to the compounds into which it enters, lead to the conclusion that a certain quantity of work, represented by a certain quantity of heat, has to be done in order to bring free nitrogen to the condition in which combination is possible. The chemist explains this by saying that the condition of free nitrogen is that of two atoms joined to one another to form a molecule and requiring the expenditure of a certain quantity of heat to tear them apart and leave each atom free to enter into new combinations.

The most prominent source, perhaps the only true source, of nitrogenous compounds in nature is found in the union of nitrogen and oxygen of the air under the influence of the electric discharge as in lightning, etc. Nitric acid is washed down from the air by rain during a thunder storm, either free or as ammonium nitrate or nitrite, and these substances, and ammonia, the product of their reduction, are the starting points of mineral, vegetable and animal compounds containing nitrogen. The conversion of nitrogen of animal and vegetable matter into ammonia and nitric acid under the influence of bacterial life is a secondary process and does not deal with free nitrogen.

Whether the union under the influence of the electric spark be purely a heat effect, or whether it results in part from a special polarity impressed upon the atoms of nitrogen by the discharge, it is now definitely proven that heat alone in presence of a strongly basic substance, like an alkali, is sufficient to effect the combination of nitrogen and carbon. The discovery, made accidentally, that the hot blast iron furnace fulfils at times the conditions necessary for the production of cyanogen from nitrogen of the air, was the beginning of a series of experiments upon the fixation of free nitrogen which have cast much light upon the nature of the problem.

Nevertheless, the conditions of the blast furnace furnish the best basis for the study of the question, and most of the early attempts to fix atmospheric nitrogen as cyanogen have striven to imitate these conditions more or less closely. Bunsen indeed (p. 19) suggested the construction of a furnace on the plan of the blast furnace for production of cyanides only, but it is difficult to see the practicability of such a plan unless the size of the furnace were very much reduced or the yield of cyanides very small as compared with consumption of fuel. We have to inquire then, what are the essential and what the non-essential conditions for the fixation of free nitrogen as cyanogen? The investigations of the blast furnace itself with this object has been done by Bunsen and Playfair (p. 13), and the various forms of apparatus which have been applied to the manufacture of cyanides upon this plan and the experience drawn from them furnish much additional material for such an inquiry.

We are limited here to the study of the synthesis of cyanogen, but the conversion of the nitrogen of the air into ammonia or cyanogen on the one hand, or into an oxide of nitrogen on the other, are mere phases of the great question of the fixation of nitrogen, and as the synthesis of one of these substances by the aid of atmospheric nitrogen would lead to the production of all, this limitation cannot exclude all considerations of these related substances.

The conditions essential to the fixation of nitrogen and the production of cyanides are indicated in the operation of the blast furnace, but only in the most general way. Neither observations nor experiment with the blast furnace have yet enabled any one to control it for the production of cyanides. The appearance of cyanides as a product of these furnaces, whenever observed, has occurred unexpectedly and has generally ceased as suddenly and mysteriously as it began. Bunsen's proposal, to erect a furnace similar to a blast furnace to be worked for cyanides only, has never been fully acted upon, and in the light of present experience it offers little promise of success. We have learned from the study of the blast furnace only that a high temperature, a reducing atmosphere, an alkaline flux and an excess of nitrogen are conditions favorable to the process.

The conditions most suitable in respect to temperature, flow of nitrogen, quality and density of carbon or carbonaceous fuel, proportion and nature of base, etc., are as yet undefined.

The more manageable furnace of Possoz and Boissiere (p. 13) although holding rather closely to the principle of the blast furnace, is free from its greatest defects in that it has no very deep column of coal to resist the flow of gases or crush the lower portions into a compact mass by its weight. The air or nitrogen is admitted at many points also, and the cross section of the furnace is not small enough to prevent access of the gases to the centre of the column of coal. Its defects are, slowness of conversion of nitrogen into cyanogen, rapid destruction of the lining of the furnace, and contamination of the cyanides with silicates thereby formed.

The process of Margueritte and Sourdeval (p. 15) and that of Romily (p. 24) are each, for a different reason, free from the chief of these defects, yet they have been no more fortunate than their predecessors in finding a practicable, commercial process.

In order to reach a conclusion as to the present aspect of the whole question, it may be well to take up and consider in detail the various conditions upon which the absorption of free hydrogen by carbon depends, to see how far the theory of chemistry may lead us in anticipating the effect of each and to find, if possible, what combination of conditions gives, in the light of theory and past experience, most promise of success.

1. The Influence of Temperature.

Possoz and Boissiere (p. 13), to whom great deference is due as the authors of the most persistent as well as the most sucsessful efforts ever made in this field, give unqualified testimony, as the result of long experience, to the necessity for very high temperatures. A white heat is said to be required and the fixation of nitrogen, other things being equal, is directly proportional to temperature. On the other hand, Armengaud and Ertel both claim that lower temperatures are quite adequate to effect the combination of nitrogen and carbon. Walter Weldon, also, one of the foremost authorities in the application of chemistry to manufactures of this or of any age, stated, in 1879, as the result of his own experiments, that the limit of temperature in this operation had been placed too high and that a red heat was sufficient. Siepermann, in 1887, testified to the same effect, basing his views on a series of experiments.

The question at issue relates only to the difference between a cherry red and a white heat, but this difference is of the utmost importance in the practical operation of a plant, and may of itself be the point upon which the whole question will ultimately turn. It is possible, however, that, under conditions, either of the above views may be correct and the question must remain an open one until the process shall have been more fully studied.

2. The Influence of Oxygen.

Is is generally admitted, as the result of all experiments upon the manufacture of cyanides, that oxygen and cyanogen cannot exist together at high temperatures. Theory leads to the same conclusion. Cyanogen is a combustible substance and the effect of oxygen upon cyanides is either, in the case of the alkaline cyanides, to convert them, first into cyanates and then into carbonates, or in the case of cyanides of the heavy metals, to decompose them with liberation of carbon monoxide and dioxide. All processes, therefore, using air as a source of nitrogen, provide for absorption of oxygen or its conversion into oxides of carbon. The mixed gases of the cyanogen furnace must be as a whole reducing, not oxidizing, in character.

3. The Influence of Water.

Here again we have P. and B. (p. 13) with their weight of practical experience insisting upon a condition which receives little support from others. It is evident, however, that the conditions of their furnace did not prevent the exclusion of moisture to such an extent as to decide the question absolutely, and the ill effects of water when admitted purposely and in greater quantity may be ascribed, in great part, to its cooling effects merely, when we remember the great expenditure of heat under which water is decomposed by carbon. Water in excess, also, decomposes cyanides, yielding ammonia. The experiments of Langlois are quite conclusive as to the principle that water in moderate quantity does not influence the production of cyanides, and Armengaud, Ertel and others (p. 15) speak positively as to its advantages. If the formation of ammonia is a preliminary stage in the synthesis of cyanogen, as Kuhlman suggests (p. 22), the presence of hydrogen, or, what is in effect the same, of vapor of water, is a necessary condition. Vapor of water is an oxidizing agent under certain conditions of temperature and for certain elements, but it is possible that cyanogen is not attacked by it at high temperatures in presence of hot carbon, carbonic oxide or hydrocarbons. The conclusions of several experimenters that water does not hinder the formation of cyanides is not, at any rate, definitely contradicted by theory.

4. Time of Contact Between Nitrogen and Carbon and Degree of Subdivision of Carbon.

If we assume that the base, which is found to be necessary in production of cyanogen from nitrogen of the air, combines instantly with the nascent cyanogen, the question of time is one simply of the speed of the preceding reaction between nitrogen and carbon. Chemical action between a solid and a gas, when the temperature necessary for the reaction has been attained, depends principally upon the surface exposed. The action may be assumed to be instantaneous like the action of oxygen upon hot and finely divided carbon and to be retarded only because the products of combustion cannot be removed from the sphere of action at the same rate at which the action takes place.

In a process like that of Possoz and Boissiere, and when each fragment of charcoal is bathed in a film of fused potash, action is limited by the rate at which the fused cyanide circulates in the pores of the charcoal and gives place to unchanged potash on the surface. New surfaces of carbon for attack, or of potash for absorption, are therefore exposed less frequently than is required, and complete saturation, that is, conversion into cyanide, is attained only after a long exposure and with much waste of gas and heat. The absorption of nitrogen is probably also retarded progressively as combustion proceeds, both because the pieces of carbon are reduced in size and therefore facilitate clogging of the flow of gas, and because the potash and fused cyanide are relatively more abundant as carbon decreases and lesser surface of carbon is exposed.

Both practice and theory, therefore, lead to the conclusion that other things being equal, the process will be hastened by any arrangement that tends to increase the surface of carbon exposed. The use of pulverized fuel would seem to be the ideal condition so far as carbon is concerned, and with an excess of ammonia, the only gaseous alkali, would probably, at a proper temperature, yield ammonium cyanide readily, as shown in Romily's experiment (p. 24) in which a smoky flame of hydrocarbon gas burning in air yields ammonium cyanide when the gas is charged with ammonia.

The effect of supplying the base also in the condition of powder would probably be to still further facilitate the action, as gaseous cyanogen would meet solid particles of highly heated base as soon as formed, and would combine with the metals of these bases to form cyanides. Alkalies would fuse and would probably tend to produce aggregations with particles of carbon, to that extent impeding access of air to them, but when we take into account the increased rapidity of chemical action under these conditions and the short time given to each group of particles in passing through the furnace, the gain by the process of pulverizing will probably be greater than the loss. Solid bases, like lime or baryta, are free from the latter objection, but also have less chemical energy.

5. Influence of Alkalies or Other Bases.

The influence of a base upon the union of carbon and nitrogen, both being in contact with the base and at a temperature sufficiently elevated for combination to occur, is probably due merely to the fact that the base serves to remove cyanogen from the sphere of action as fast as it is formed. The belief in a predisposing affinity, a non-correlated power, acting from a given centre to bring about a reaction in which the predisposing body has no share except to combine, *subsequently*, with the products of the reaction, is an ingenious fiction of the older chemistry, which finds little support at the present time. The influence of a foreign substance in impeding the union of two bodies by lessening the opportunities for contact of their respective atoms within a given time supplies a more tangible explanation. Every chemical reaction is limited in violence after the first moment of action—is impeded and finally checked—by the products of the reaction, unless these are removed. Like any foreign substance these substances impair the freedom of access of the reacting atoms to one another and absorb heat which is necessary to the reaction. Whatever tends to remove these products quickly from the field of action tends to facilitate the reaction itself. When *a* and *b* unite to form *ab*, the presence of a third substance, *c*, capable of combining with the compound *ab* to form *abc*, but not with *a* or *b* separately, will facilitate the union of *a* and *b*, for the above reasons.

This would seem to be the function of the alkali or other base in the synthesis of cyanogen. The conclusion is sustained apparently by the experiment of Langlois and the earlier chemists (pp. 10, 21–22), in which ammonia passed over hot charcoal yields ammonium cyanide. Trommsdorff first suggested that it was the presence of ammonia that favored here the formation of cyanogen by furnishing a means of fixing it as soon as formed.

The theory of the action of bases, of alkalies at least, is susceptible of another explanation. Many authorities (Bromeis, Bunsen and Playfair, Graeger, Riekeu *et al.*, pp. 7, 10, 14, 22) believe that the union of carbon and nitrogen occurs only at or above the temperature at which potassium is reduced from its oxide by carbon. Metallic potassium or its vapor must be taken into account upon this hypothesis when the reaction in question is studied. This view would explain the lesser activity of soda in forming cyanides, as it is less readily reducible. Graeger (Jsb. chem. Tech., 1858, 81) finds that in the old fusion process for prussiates the yield is lessened in proportion as potash is replaced by soda,. even at temperatures approaching the fusing point of the cast iron pot. He believes that nitrogen from the organic matter in this case is volatilized and lost before metallic sodium is formed, owing to the high temperature required for reduction of sodium. Lime and baryta, from their infusibility, are also difficult to reduce, and should be less suitable for the process. Knowing the incompatibility of cyanogen and oxygen at high temperatures and the fact that cyanogen unites directly with the metals, it is quite possible that cyanogen can only combine when the metal itself is presented to it, and cannot reduce the oxide, at least only by being itself destroyed. Bunsen and Playfair held (p. 18) that cyanogen in the upper part of the iron furnace acted as a reducing agent and was itself destroyed in reducing oxides of iron.

The theory of Berthelot (p. 16) is interesting in this connection. He holds that a direct compound of potassium and carbon (C_2K_2) is formed and that this compound absorbs nitrogen, forming with it potassium cyanide. The theory is in perfect accord with the preceding one. Delbruch (p. 10) has also showm that cyanogen is formed when a mixture of nitrogen or ammonia with carbon dioxide is brought in contact with fused potassium.

It is possible also, that potassium or other metal, under these conditions, unites directly with nitrogen to form nitrides which then combine with carbon, yielding cyanides. The observation of Brieglied and Geuter, already referred to (p. 19), that magnesium nitride, when heated with carbonic oxide or carbonic acid evolves cyanogen, lends color to this view.

6. The Nature of the Base to be Used.

As far as experiments have gone, potash seems to be the base best suited. Its great chemical energy and ready fusibility and reducibility in presence of carbon give it advantages over all other bases. Soda, besides being somewhat less powerful as a base, fuses at a higher temperature and therefore involves increase of wear and cost in apparatus. On the other hand it is cheaper, weight for weight, than potash, and, in addition, its lower molecular weight enables it to do more work for a given weight than potash in the proportion of 138.2 to 106.

The facility with which ammonium cyanide is formed when ammonia is passed over hot charcoal indicates that ammonia, like the fixed alkalies, combines very readily with cyanogen. It has the advantage of not acting as a flux upon the material of the furnace. The use of ammonia, itself produced from nitrogen of the air, to facilitate the synthesis of cyanogen at a lower temperature than that thought necessary for cyanogen alone, is suggested by Romily's experiment and may be a feature of future development in the fixation of nitrogen.

Of the infusible bases the alkaline earths, lime, baryta, strontia and magnesia only, seem to have sufficiently strong basic power to form cyanides with the air. The cyanides of other metals decompose quite readily when heated. The advantages of the alkaline earths are their infusibility, which prevents clogging of the mixture of coal and basic substance and so permits perfect access of nitrogen, and their cheapness. The corresponding cyanides are soluble and easily converted into alkaline cyanides. These qualities compensate to some extent for the deficient chemical energy of the alkaline earths. Margueritte and Sourdeval (p. 20) found that baryta absorbed nitrogen rapidly and that barium cyanide yielded ammonia on treatment with steam. Siepermann (p. 23) mixes baryta with alkalies to prevent fusion and clogging. Lime, the cheapest of these bases, seems to have been little used. Armengaud speaks of using it in his apparatus in 1843 (p. 20) and Fleck (p. 23) claimed the discovery that hot calcium hydrate could convert a mixture of nitrogen and carbonic oxide into ammonia and carbon dioxide.

7. The Relation of Ammonia to Cyanogen and the Conditions which Determine the Formation of One or the Other.

The production of ammonia by bringing together at a high temperature carbon, air or nitrogen, steam and a basic substance has long been known. The history of the subject although closely related in many respects to the question in hand has been omitted in this discussion for want of time. It is, however, difficult to separate two questions which deal, in a certain sense, with different phases of the same reaction. If any definite conclusion can be drawn from the results of industrial experiments it is that higher temperatures favor the production of cyanides and lower temperatures, of ammonia, with the addition also that vapor of water in excess is certainly unfavorable to the productions of cyanides but probably favorable to the production of ammonia. It is possible even that, for a temperature sufficiently high, supposing that it could be maintained against the cooling effect involved in the decomposition of water by hot carbon, the proportion of water above or below a given limit might be the condition determining the production of ammonia in one case or cyanides in the other. It is difficult in the present state of our knowledge upon the subject to mention any conditions, other than variation in temperature and variation in quantity of water, which can account for the production at one time of ammonia and at another of cyanides in a furnace using in both cases precisely similar materials. The belief of Berzelius, Wöhler, Bromeis and others (pp. 7, 9), that formation of ammonia was the preliminary stage in the synthesis of cyanides and that water acted as an intermediary, accords with this view. An excess of water both by lowering the temperature and by impeding contact of nitrogen and carbon would retard the formation of cyanides and proportionally increase the ammonia.

The extraordinary permanence of ammonium cyanide, in comparison with other ammonium salts, at high temperatures (p. 22), (taken in connection with the fact that ammonia by itself is dissociated at high temperatures) may indicate that at very high temperatures ammonia can resist dissociation only in presence of a more refractory substance, hydrocyanic acid, with which it can combine. Ammonia in contact with coal, at a very high temperature, forms ammonium cyanide (p. 21, 22). This may be taken to mean that ammonia is more unstable in presence of hot carbon at that temperature than when merely heated alone, and that the portion first decomposed forms hydrocyanic acid which unites at once with a portion of ammonia not yet decomposed (because not yet in contact with not carbon), and thus, in forming the stable compound ammonium cyanide, the ammonia is protected from dissociation or chemical decomposition. But if ammonia is *decomposed* at these temperatures it is unlikely that it can *form* under the same condition, while it is evident that cyanogen not only can but does form. We are led then to the hypothesis that, other conditions remaining unchanged, temperature is an important, if not the leading condition, which determines the production, respectively, of ammonia or cyanogen.

With respect to water as a determining cause, it may now be said that while an excess of water probably tends more and more to oxidize or otherwise decompose cyanogen[1] as fast as it is formed at very high temperature its influence would be merely mechanical in retarding the formation of ammonia at a temperature somewhat lower. When the temperature is sufficiently high to enable carbon to decompose water one of the products of decomposition (CO) is without influence upon the formation of ammonia, while the other, hydrogen, is in the nascent state and therefore in the condition most favorable for union with nitrogen irrespective of the presence of carbon. *If water were in a state of dissociation due to heat alone*, oxygen coming from water could not, under those conditions, act upon ammonia, since it could unite neither with hydrogen or nitrogen. The case may be stated as follows :

a. Ammonia is not permanent at very high temperature, except in combination with cyanogen but *is* permanent at somewhat lower temperatures, still above a red heat. It is not decomposed by water at any temperature, but at certain temperatures its formation will be favored by the very conditions that make water an unstable compound, *i. e.*, high temperature and presence of carbon.

b. Cyanogen is permanent at very high temperatures with or without presence of ammonia. Cyanides are probably decomposed by water in excess at very high temperatures.

Finally, *the presence of water in moderate quantity* at certain elevated temperatures may favor the production of cyanides by permitting a certain formation of ammonia which is then converted into cyanides, the temperature being lower on the whole than that required for the formation of cyanogen without water. Here ammonia clearly acts as an intermediary, but the temperature, being above a certain limit, favors the production of cyanides rather than ammonia as the final product. At a slightly lower temperature—still, however, above the point at which water is decomposed by carbon—ammonia would form in preference to cyanides and in greater quantity ; with an excess of steam ammonia would

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[1] Karmrodt found that steam passed over hot potassium cyanide caused evolution of ammonia and the heated residue no longer contained cyanogen.

be the sole product. This may suggest the possibility of working a furnace intermittently with changes of temperature for the production in succession of cyanogen and ammonia or, what is the same in principle, the working of two furnaces in conjunction, one to produce ammonia and the other to convert this ammonia into cyanides.

8. The Influence of Other Gases Upon the Absorption of Nitrogen by Carbon.

The influence of carbon monoxide and carbon dioxide cannot be definitely stated. Bramwell expressed a preference for the latter in his cyanogen retorts, along with nitrogen, but it is hard to find any reason in theory for this preference, since the higher oxide of carbon is always reduced to the lower in presence of hot carbon and must be so changed in the cyanogen furnace. As it is therefore, an oxidizing agent, it should in theory, be more objectionable than carbon monoxide. It is more probable that foreign gases, provided they have no oxidizing character, merely impede the access of nitrogen to carbon and only act mechanically to retard the union of carbon and nitrogen.

It may perhaps be expected that the above theory should also explain why cyanogen is not formed in a coal fire by simple union of carbon and nitrogen. In the first place it has never been definitely settled that it does not. Many authorities (Binks, R. Wagner, Brunquill) have held with greater or less force to the belief that it does, or at least that it may so form under certain conditions. That it does not form readily or abundantly must, however, be conceded. Again the instability of cyanogen itself may be such, under the conditions of an ordinary fire, that it is decomposed as fast as formed, and its instant fixation by combination may be essential to its formation in appreciable quantities. The effect of fire gases, carbon dioxide or monoxide, sulphur dioxide, etc., upon free cyanogen has never been investigated, although several of the authorities already quoted have, from their own experience in the synthesis of cyanides, indicated a belief in the influence of one or other of these gases upon the process (p. 15-16).

9. The Influence of Hydrocarbons in the Preparation of Cyanogen or Ammonia.

If hydrocarbon gases or vapors of heavy hydrocarbons were brought into a furnace containing the materials for production of cyanides or ammonia, namely, hot coal, nitrogen, water in greater or less quantity and an alkali or other basic substance, the result would be a partial decomposition or dissociation in which carbon, and hydrogen would be set free, and fixed gases having the composition of the lower paraffines or olefines would remain. Heavy hydrocarbons, oils like crude petroleum, might be used in part to supply the carbon necessary to the reaction ; being in a condition of most minute subdivision as set free from combination, it would be most suitable for rapid combination. It is possible also that hydrogen liberated at the same time and in the nascent state would be better adapted to the synthesis of ammonia than at any other time, and further, this hydrogen would be obtained at less expenditure of heat than hydrogen from decomposition of water by carbon. The condition of a furnace fed with hydrocarbon vapors would resemble to a great extent the smoky gas flames of Levoir and Romily, (p. 23–24) in which ammonium cyanide was produced even without the intervention of a base other than ammonia.

10. The Influence of Pressure.

The data derived from experiment on the large scale give little information upon this point. Newton remarks (p. 11) that the production of cyanides is improved by a certain pressure and by friction between the solids and gases of the furnace, but this remark applies to very low pressures such as depend merely upon friction in retarding the gases as they are drawn or forced through the alkalized charcoal by a pump. There is no evidence of systematic use of high pressures, exceeding one atmosphere for example, and the furnaces thus far designed for making cyanides or ammonia are none of them adapted to the use of pressure. It is possible that the necessary reaction would be much assisted by pressure. There is every analogy indeed to favor this view. Combustion in compressed air or oxygen is more rapid than at normal pressure; and the union of nitrogen and carbon should be also accelerated. More of the unlike particles are brought in contact in a given time, and the opportunities for combination being multiplied combination should occur in the same proportion. Moreover the heat lost in expansion of gases is lessened and the temperature within the furnace should be more readily maintained.

If it were possible to maintain a pressure of several atmospheres within a furnace while the gaseous contents of the furnace were continually supplied and discharged, there is every reason to believe that the furnace would be more economical and more effective in the production of cyanides or ammonia.

SUMMARY.

The present aspect of the question may be summarized as follows:

The manufacture of cyanides and ammonia from the nitrogen of the air, while quite possible on the small scale, is beset with difficulties in its economical and commercial application, which, up to this time, have been insurmountable. These difficulties are probably matters relating mainly to construction and to endurance of materials.

At the same time there is still much uncertainty in regard to the chemical and physical conditions most favorable to the fixation of nitrogen.

The following conclusions are the result of the foregoing inquiry:

1. The temperature necessary for formation of cyanogen may be lower than at first supposed, but certainly not below a high red heat. For ammonia a low red heat is sufficient.
2. The presence of free oxygen is deleterious in all cases.

3. Water in very small quantities is not prejudicial to production of cyanogen, and an excess is probably necessary in the synthesis of ammonia.

4. The long-continued contact of carbon and nitrogen is of less importance than thorough commingling of all reacting materials.

5. The presence of a strong base is essential, but under certain conditions ammonia, produced synthetically, may serve the purpose of a base and effect the synthesis of ammonium cyanide.

6. Alkaline bases are preferable, potash especially, and probably because of the intermediate action of metallic potassium, which is reduced at a lower temperature than sodium. Baryta is the best of the alkaline earths for the purpose.

7. Ammonia and cyanogen are probably formed under conditions differing in respect to temperature and moisture, but otherwise similar, as already indicated. (2.)

8. The presence of carbonic oxide and of reducing gases in general is probably favorable, while oxygen, carbonic acid and steam in excess (the latter only in the case of cyanogen) are probably injurious. Nothing is known as to the influence of sulphurous acid or hydrogen sulphide, but they are probably undesirable.

9. The presence of hydrocarbon vapors is favorable, and may, under certain conditions, permit the formation of both cyanogen and ammonia without the presence of a base.

10. There are no direct data for estimating the influence of pressure upon the reactions in question. The application of pressure is at least worthy of trial.

DISCUSSION.

Dr. Waller said that the so-called "catalytic action" afforded no explanation of the effect of certain elements in the cyanogen forming process, and mentioned the apparent inducements offered for the production of a salt by the presence of a base, as for instance, the formation of calcium chromate by heating chrome iron ore with lime.

Dr. Alsberg called attention to the fact that addition of lime would in some cases contribute merely physical conditions which would aid in the reaction, such as porosity, infusibility, etc. Also that frequently in such instances of so-called catalytic action the temperature of formation and of dissociation of the new compound are so nearly the same that unless a base is present to unite with and retain it, as a salt not dissociated at that temperature, no reaction results. He expressed it as his opinion that not even a momentary formation of such compounds takes place under such temperature conditions unless in the presence of a base to retain them. The addition of iron in the cyanogen process has something to do with its success—as in the Castner sodium process.

Dr. Doremus referred to the production of oxygen from $KClO_3$ and MnO_2, and to a paper published in the *Chemical News* intended to show the existence of a number of definite successive reactions between these substances. Experiments made with indifferent substances—*e. g.*, sand—substituted for MnO_2, gave dissimilar results.

Mr. Sabin : The escape of nitrogen as ammonia in the old prussiate process may be very great if the management is unskillful. A cyanide is first formed and then, at a higher temperature or on prolonged heating, ammonia is produced. I believe that in a properly constructed and continuonsly acting furnace all of the nitrogen of leather scrap could be converted into ammonia in presence of caustic soda and moisture, although the process might not be economical. I doubt whether any cyanide manufacturers in this country, with one exception, are making a paying business of it, as such large quantities of cyanides and ferrocyanides are imported. The exception, a firm in Newark, are using an improved pear-shaped retort heated only at the central wide portion.

Dr. Alsberg : We are on the eve of a complete revolution in prussiate processes ; cyanides and ferrocyanides are manufactured in Germany from gas purifier waste in such quantities as to have reduced the price 25 per cent. The process of making cyanides from sulphocyanides is not easy because of difficulty of eliminating sulphur. The only practical process at present is by heating sulphocyanides and finely divided iron under pressure at 120–140°C., whereby ferrocyanide and ferrous sulphide are formed. It is also stated that if a sulphocyanide and ferrous sulphate are mixed and exposed to air, that sulphur is gradually taken up in presence of free alkali, but it seems somewhat doubtful. The old method of making cyanides will have to be abandoned for cheaper methods. Sodium ferrocyanide is now made in large quantites to replace potassium ferrocyanide using gas house wastes and commercial soda ash. More of sodium bichromate is used in dyeing and calico printing than of potassium bichromate, but certain colors, it is claimed, will not permit of the substitution.

Dr. Doremus said the Wilkinson process for manufacturing wood gas produced little cyanogen and no ammonia; in fact he had never heard of either as impurities requiring any attention.

Prof. Breneman: The formation of ammonia by an ordinary coal fire may not be impossible. In the gas retort the amount of ammonia and cyanides produced is very large, possibly larger than that due to the nitrogen in the coal alone, although the access of atmospheric nitrogen, through leakage and at time of changing, cannot be very free.

[*] In regard to the question of action by presence or predisposing affinity, the case, in its strictest sense, is inconceivable. It involves action *for a purpose* by inanimate things. Also, the supposition that action of a certain kind cannot take place, even momentarily, under conditions in which decomposition also occurs, is a necessity only in theory. It presupposes that every newly formed molecule is instantly solicited by all of the conditions, chemical and physical, that affect the mass, whereas in a reacting mass of *solids* (less so in the case of liquids or gases, although still existing) there are difficulties in the way of instant diffusion of all conditions. Heat may be locally increased or decreased momentarily by chemical action, and *vice versa*, and these changes may favor the local formation of products which are instantly fixed by active substances present in excess, as has been already explained (p. 38).—A. A. B.