THE PREPARATION
of
CARBON MONOSULPHIDE AND HYDROCYANIC ACID
by the use of
ACTIVATED CARBON

Thesis

by

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INTRODUCTION

During the late war a great deal of work was done in this country on the development of an "active" form of charcoal for use in gas masks as an adsorbent for certain toxic gases. A large amount of this work was done in the laboratories of the National Carbon Company, with the result of a large scale method for producing from whatever source of C-bearing material might be cheapest or most desirable, an amorphous form of carbon called "activated carbon".

Active carbon is formed whenever carbon is deposited at a relatively low temperature by a chemical or thermal decomposition of C-bearing materials, generally below 600-700 degrees C. A similar decomposition carried on under higher temperature conditions gives another form of carbon called "inactive carbon" because of its stability toward oxidizing agents and its low specific adsorptive power.[1]

The first product occuring in the low temperature distillation of carboniferous materials is a stabilized complex of hydrocarbons adsorbed on a base of active carbon. Active carbon is obtained from this by freeing the hydrocarbons, which may be accomplished in two different ways:

a) by a process of controlled distillation, and

[1] N. K. Chaney, Trans. Em.Electrochem.Soc., 36, preprint (1919)

b) by a process of differential oxidation.

The latter gives the most satisfactory results and may be applied to a wide variety of primary carbons.

The active carbon used in the work described by this paper was selected from a sample furnished by the U. S. Fixed Nitrogen Research Laboratory and was activated from a cocoanut shell base. It was thought that this new form might have special reduction effects that would not be found in an ordinary wood charcoal reduction, and hence its effect on two substances was tried.

(1) $C+CS_2 = 2\ CS$)
) (Ideal)
(2) $C+NH_3 = HCN+H_2$)

The value of the product in (1) is more theoretical than practical, because of the fact that it has never been prepared in quantity. However, its nature would lead one to surmise that it might find application in gas warfare as well as in medical and fumigation work if it could be produced on a commercial scale.

The value of HCN from (2), however, is distinct, particularly in Southern California, where a large market for the liquified form of the gas for use in citrus tree fumigation has grown up in the past few years. The HCN produced by the treatment of NaCN with H_2SO_4 has a market value of about 75¢ per lb. If large enough yields at reasonably low temperatures could be secured by the reduction of NH_3, the relatively low cost of the

two raw materials and the absence of any waste product (there is a good market for H_2) such as impure Na_2SO_4 would furnish a more economical method of HCN production.

PART A-THE REDUCTION OF CARBON DISULPHIDE BY ACTIVE CARBON

I - PREVIOUS WORK.

A number of attempts to prepare CS have been made in the last 65 years. The record of this work is very unusual in that it is simply a succession of reports of supposedly successful attempts to make CS, followed a few years later by other work which disproves the previous assertions.

In 1857 Baudrimont[1], a Frenchman, did the first work on CS. He claimed that he produced the gas in a number of ways, chief among which were the decomposition of CS_2 at high temperatures either by leading it as a gas over glowing Pt or pumice or by treating with hot H_2 gas, and the decomposition of CS_2 vapors by wood charcoal and all kinds of animal charcoal when broken into small bits.

Several years later, Berthelot[2] and Playfair[3] disproved the above assertion of CS_2 decomposition by Pt and pumice at red heat, and held that CS_2, when heated strongly, gave only C, S, and CS_2 vapor.

In 1875, Sidot[4] declared that he had obtained CS in a solid form by the decomposition of CS_2 in sunlight,

1 Baudrimont, Compt. Rend., 44, 1000, (1857)
2 Berthelot, L'Institute, (1859), 365
3 Playfair, Jour. Chem. Soc. London, 13, 248
4 Sidot, Compt. Rend., 81, 32,(1875)

using certain metals as catalysts[1]. S. Kern in 1876 showed that the solid reddish substance obtained thus was due to the iron catalyst used.

Deninger[2] claimed to have prepared gaseous CS by treatment of chloroform and iodoform with Na_2S and Ag_2S respectively, and also by the action of sodium on a mixture of CS_2 and analine. The resulting gas was identified by explosion and subsequent measurement of the ratio of SO_2 to CO_2, but this work was disagreed with by Russell and Smith[3] and by Dunn[4].

Julius Thomsen[5] tried to carry out the reaction between CS_2 and Cu in two stages, the first giving CS and the second C and CuS. He claimed to have obtained a large yield of CS, but Stock and Kuchler[6] showed this belief to be due to an error in the construction of his apparatus.

The most recent work has been done by Dewar and Jones[7], who obtained solid CS from the reaction

$$X\ Ni(CO)_4 + X\ CSCl_2 = NiCl_2 + 4\ X\ CO + (CS)_x$$

[1] This experiment of Sidot's was repeated qualitatively without the use of a catalyst, but using a quartz container in order to get ultra-violet light on the CS_2. After several weeks of exposure, a fairly heavy, reddish-brown precipitate was observed which answered the description given by Sidot of his solid CS.

[2] Deninger, Jour.Pr.Chem., 51, 346, (1895-2)

[3] Russell & Smith, Jour.London Chem. Soc. 81, 1538

[4] Dunn, Proc. Chem. Soc. of London, 26, 116.

[5] Thomsen, Zeit, Inorg. Chem., 34, 187, (1903)

[6] Stock & Kuchler, Berichte, 36, 4336.

[7] Dewar & Jones, Proc. Royal Soc. of London, (A) 83,408.

L. C. Martin[1] gave evidences in the form of photographs and wave lengths of some bands supposed to be due to CS formed in the vacuum discharge in CS_2 and by S in a C arc.

From the above summaries and from work done in 1915 by Lewis and Lacey[2], it seems probable that CS exists in both gaseous and solid form, the latter being a polymer of the gas. Of the various methods of preparation of the gas, one of the few which was not refuted was the original one of Berthelot by which he decomposed CS_2 vapor with charcoal. Hence, it was decided to try this method under more modern conditions and using activated carbon as the reducing agent.

II - METHOD

It is probable that CS exists and corresponds to CS_2 as CO corresponds to CO_2, and also that CS is an easily polymerized gas which is, however, not condensable at liquid air temperatures[2]. The difficulty in forming gaseous CS lies in the endothermic character of both sulphides. The heat of formation of gaseous CS_2 from amorphous C and solid S is given by Landolt-Börnstein as - 26000 cal. and that for CS under similar conditions by Thomsen[3] as - 28000 cal.

Such compounds require high temperatures for pro-

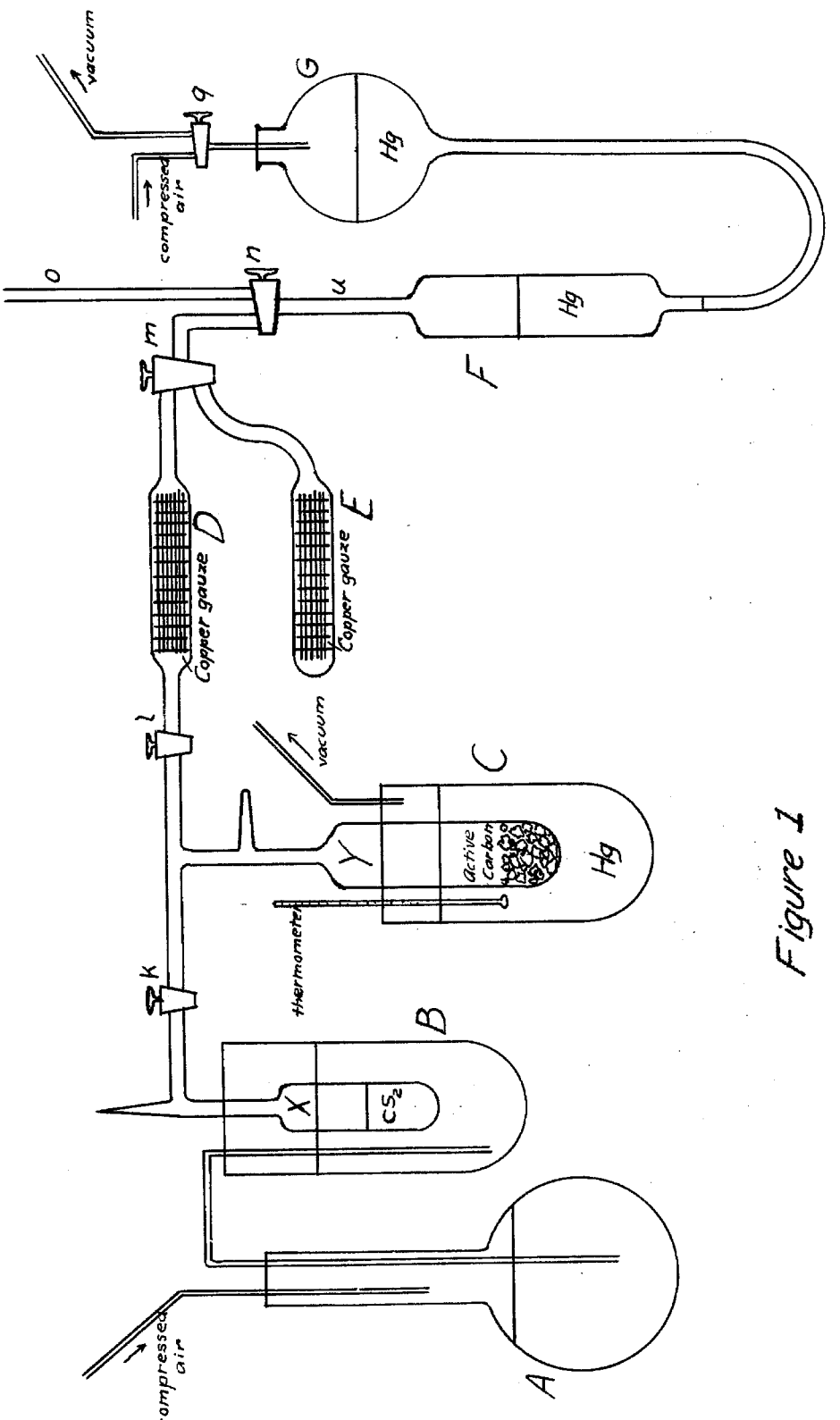
1 L.C.Martin, Proc.RoyalSoc. of London, (A), 89, 127.
2 Lewis & Lacey, Jour. Am. Chem. Soc., 37, 1976, (1915)
3 Julius Thomsen, Zeit. Inorg. Chem., 34, 187, (1903).

duction from the elements, but they may also be obtained by breaking down other compounds. It seems probable, therefore, that the best way to form CS is by the suitable breaking down of CS_2. To accomplish this end through the reaction

$$CS_2 + C = 2\ CS,$$

using activated carbon as the reducing agent, the apparatus shown in Figures 1, 2, and 3 was designed and set up.

The proposed use of the apparatus was as follows: In tube X was placed the liquid CS_2 and in tube Y the active carbon. Tubes F and G comprised a mercury pump by which the mercury in F was raised and lowered by alternately turning compressed air and vacuum into G. As it was raised and lowered, the three-way stopcock was first turned so that the air in F was expelled through o and then so that the air in the rest of the apparatus was sucked into F, after which it was again opened to o and this air expelled. By repeating this cycle a number of times a fairly good vacuum was obtained within the apparatus.


vacuum
compressed air
q
G
Hg
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F
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Copper gauze
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C
Y
Active Carbon
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thermometer
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CS_2
compressed air
A

Figure 1

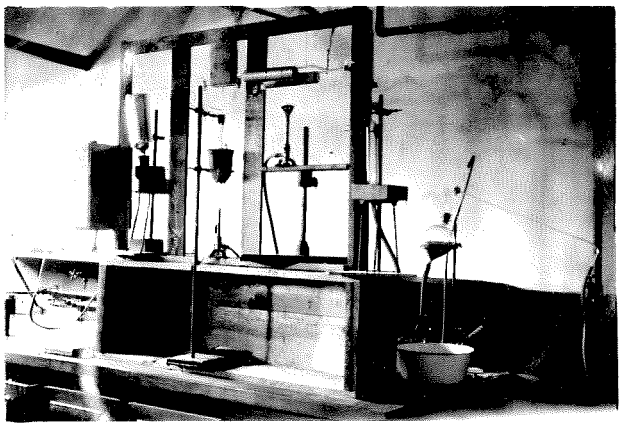

Figure 2

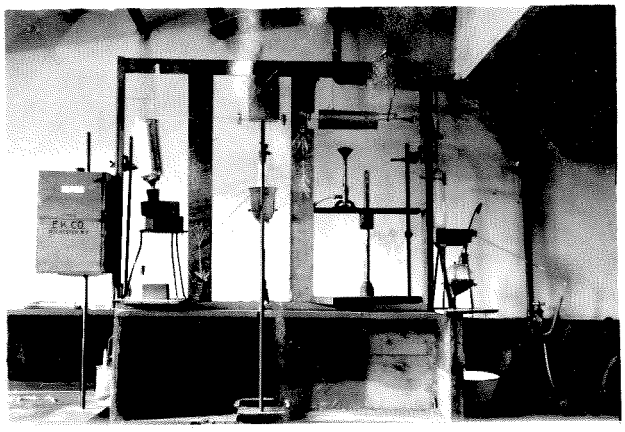

Figure 3

One essential to the success of this apparatus is that no O_2 be present, as it would complicate matters by contaminating the product with CO, CO_2, COS, and other undesirable gases which would render the separation and measurement of the CS very difficult. The active carbon contained a large amount of absorbed materials such as H_2O and O_2 which had to be removed before the CS_2 was introduced. In order to get rid of all the O_2 in the apparatus, the CS_2 in tube X was first frozen by means of the liquid air in bath B, which was pumped by compressed air from container A. Then the reaction chamber Y was heated to 300 degrees C for about six hours by means of the Hg bath C, the Hg vapors being drawn off at v. During this time the whole apparatus was evacuated as completely as possible by the mercury pump. There still remained, however, a small amount of oxygen, which was removed by heating tube D, which contained copper gauze, to about 350 deg. C by means of a tubular metal air bath. This caused the O_2 to be removed as black CuO and Cu_2O, which was deposited on the copper gauze.

The two-way stopcock l was then closed and that at k opened, and the liquid air container removed from the CS_2 tube, which was then gradually brought to a temperature of 35 deg. C by immersion in a di-ethyl ether bath. This gave a high vapor pressure of CS_2 (whose b.p. is 46.2 deg.C) throughout both tubes X and Y. Stopcock k was then closed, thus giving a definite vapor pressure of

CS_2 and weight of active carbon in the reaction chamber Y.

This mixture was then heated at constant temperature for several hours, during which time any reaction between the two substances took place. After this, stopcock k was re-opened and the CS_2 reservoir again surrounded with liquid air, which drew over any CS_2 vapors that did not react and disposed of them as solid CS_2. CS is not affected at liquid air temperatures according to Lewis and Lacey.

Then stopcock 1 was opened and the CS resulting from the reaction was drawn by means of the mercury pump into the small tube u (the copper gauze in D had been allowed to cool), whence it was forced into the reservoir E by reversing a stopcock m. The process was repeated several times until all of the gas had been drawn over.

The gas may then be measured and led out through the exit tube o and identified by explosion and consequent measurement of the ratio of CO_2 and SO_2. A rough indication of the presence of CS may be afforded by the heating of the copper gauze in tube E, which is similar to that in D. If a previous blank run shows no black coloration on the copper due to CS_2, it is reasonable to suppose that any black color which may result is due CS, which is known from the work of Lewis and Lacey to react with Cu:

$$CS + Cu = CuS + C.$$

The only other possibilities for contamination of the CS produced would be from the decomposition of the CS_2 in the reaction tube to give carbon and gaseous sulpher and the decomposition of the oxides of copper formed in D. The following caluclations show the absence of any possibility of the presence of S_2 gas from the decomposition of the CS_2, and even if some were formed in this way, it would be removed as solid by the liquid air,

$$CS_2(gas) = S_2(gas) + C \text{ (amorph.)} + 12500 \text{ calories.}$$

K (823 deg.C) for this reaction $= (S_2)/(CS_2) = 7.8 \times 10^{-2}$

Then, from Van't Hoff's law,

K (300 deg.C) $= 8.5 \times 10^{-6}$

Thus, if the pressure of the CS_2 were assumed to be 600 mm in tube Y, the maximum pressure of any sulpher vapor from its decomposition would be 5.1×10^{-3} mm, which conclusively shows the absence of any chance of contamination from this source.

Any probability of the CuO and Cu_2O decomposing to give off O_2 is precluded by the data of Foote and Smith[1] on the subject.

CuO dissociates 1% at 1000 degrees C.

Cuo dissociates <1% at 900 degrees C.

III - EXPERIMENTAL

The apparatus as outlined was completely set up and

[1] Foote & Smith, Jour.Am.Chem.Soc., 30, 1344, (1908).

tests made as to the efficiency of the mercury pump and everything was in readiness to begin making runs when it was learned that liquid air could not be obtained from the expected source. As the essential separation of CS from CS_2 depended on the freezing of the CS_2 (which can not be accomplished by any ordinary freezing medium because the f.p. of the substance is -116 deg.C), it was decided to abandon this problem for the time being and to take up the work on active carbon and ammonia.

IV - SUMMARY

1 - A complete apparatus was designed and constructed for the carrying out of the reduction of carbon disulphide by active carbon, but no experimental work could be done because of the failure of the liquid air supply.

PART B - THE REDUCTION OF AMMONIA BY ACTIVE CARBON.

I - PREVIOUS WORK

There seems to have been very little work done on the reaction between NH_3 and C, about the only work of any importance on this subject having been reported by G. A. Voerkelius[1]. He describes the results obtained by leading a mixture of NH_3 and H_2 or illuminating gas in varying proportions and at varying speeds over wood charcoal heated to different temperatures. The purpose of the H_2 and illuminating gas was simply to dilute the ammonia. He first observed the formation of HCN at 700 deg.C and obtained a maximum yield of 38% HCN at 1000 deg. C. The percentage of HCN and undecomposed NH_3 increased with the rapidity with which the gas mixture was passed over the charcoal and also with increasing dilution of the ammonia.

With these results as a basis for comparisons, very interesting conclusions can be drawn as to the relative effects of activated and ordinary charcoals on the reaction.

II - METHOD

When NH_3 is led over hot charcoal, a number of reactions are possible:

[1] Voerkelius, Chem. Zeit., 33, 1090, (1909)

(1) $C + NH_3 = HCN + H_2$

(2) $C + NH_3 = 1/2(CN) + 3/2H_2$

(3) $NH_3 = 1/2N_2 + 3/2H_2$

(4) $HCN = C + 1/2N_2 + 1/2H_2$

Of these possibilities, it was decided because of limited time to analyse only for NH_3, HCN, and $(CN)_2$.

To this end, the apparatus shown in Figures 4 and 5 was designed. Into tubes A, B, and C are pipetted definite amounts of standard acid, $AgNO_3$, and NaOH solutions respectively. One gas of the mixture coming from the combustion chamber F is absorbed in each of the three tubes. NH_3 is taken out in A, HCN in B, and $(CN)_2$ in C. The acid selected for A was sulphuric because of its low vapor pressure as compared with the other common acids. There is consequently less liability of sulphate ion passing over into the silver solution and causing contamination. AgCl would be almost sure to precipitate if HCl were used in A.

When the gases are passed through A, only the NH_3 will be absorbed because of the acid character of both the HCN and the $(CN)_2$. In B all of the HCN will be ppt. as AgCN, with the $(CN)_2$ passing on to be absorbed in the NaOH solution in C. The absorption tubes used were of special design (D of Fig. 4) which proved very effective. The incoming gases were led down nearly to the bottom of the entering tube where they were bubbled out through

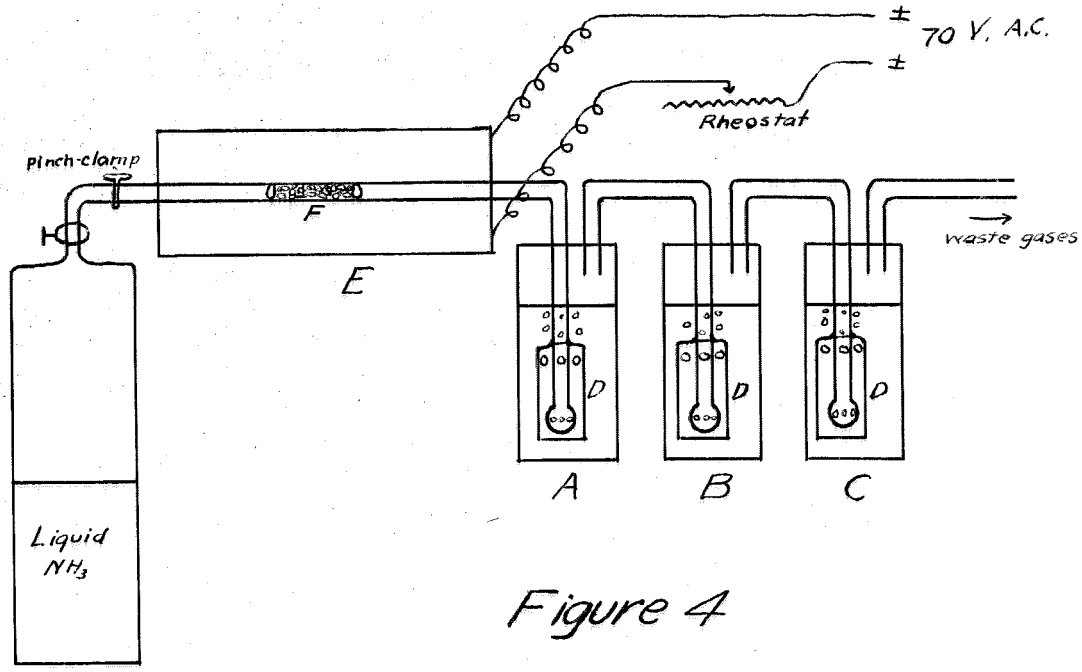

Figure 4

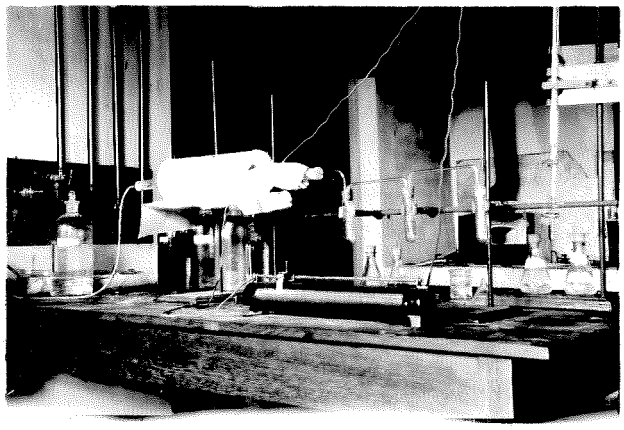

Figure 5

small holes into another slightly larger enclosed space, at the top of which were more holes which still further broke the gas up as it escaped finally into the main body of the tube. These upper exit holes were made alternate with the lower ones in order that better breaking up of the gas might be obtained. By means of a small capillary opening in the tube just before entering the absorption tubes, supplemented by a pinch-clamp, quite even bubbling was obtained. As a cylinder of liquid NH_3 was used for the NH_3 source, the back pressure necessitated by this arrangement was no drawback.

The methods of analysis used for the resulting solutions in tubes A and C were volumetric, and that for B was gravimetric. The excess acid of A was titrated ag against standard NaOH and from this the amount of acid used in neutralizing the NH_3 and the amount of NH_3 were calculated. In obtaining the amount of $(CN)_2$ caught in the NaOH solution in C, $AgNO_3$ was used to titrate against it. When this is added with constant stirring to a basic solution containing $(CN)_2$, no permanent precipitate of AgCN occurs until all of the $(CN)_2$ has combined with the sodium and silver ions to form a soluble double salt, (NaCH, AgCN). With any excess of silver ion, a permanent precipitate of AgCN occurs the appearance of which marks the end point of the titration. The basic solution of the cyanogen is diluted from 10 to 20 times with water

before the titration in order to prevent too great a concentration of base.

The mixture resulting from B was filtered and washed, thus removing all of the AgCN. The remaining Ag in the filtrate is then precipitated as AgCN in a slightly acid solution and measured gravimetrically in a Gooch filter. From this and the known amount of Ag added to tube B at the beginning of the run, the amount of HCN may be readily calculated.

The furnace used was of the simple electric resistance type with two units connected in parallel across 70 volts A.C. A 12 amp. rheostat was connected in series with the line for temperature control. With all the resistance in, a temperature of 425 deg. C was obtained as a minimum, while a maximum of 750 deg. C could be reached. The combustion tube used was of Pyrex glass, and the active carbon, in order to obtain the best contact possible, was packed loosely in a space about 6" long and completely filling the cross-section of the tube, being held in place by asbestos plugs. This part of the tube was then centered in the furnace where the temp. was the most uniform. The tube was packed and sealed in at the end of the furnace by shredded asbestos in order to prevent circulation of air and consequent uneven heating in the furnace.

III - EXPERIMENTAL

A total of seven runs under varying conditions was all that time allowed. In tabular form, the results obtained appear as follows:

Run #	Duration (min.)	Temp. (deg.C)	NH_3 (g)	HCN (g)	$(CN)_2$ (g)	Total N_2 (g)	N_2 in HCN as % of Total N_2	Remarks
1	75	425	---	---	---	---	---	Qualitative run
2	90	425	2.765	Traces	None	---	Traces	---
3	75	500	2.725	0.0115	"	2.251	0.265	---
4	70	600	2.395	0.0141	"	1.978	0.370	---
5	60	600	2.680	0.0205	"	2.217	0.470	Easterrate of bubbling
6	60	600	2.215	0.0187	"	1.835	0.528	Dil.with ill.gas
7	60	725	1.740	0.284	"	1.580	9.325	---

The first run was primarily a qualitative one for the purpose of determining the concentrations of the solutions necessary for the three absorption tubes. It was found, using N/2 H_2SO_4 in A, that a slight white ppt. formed in B at the start of the run which later became fainter and finally disappeared entirely. This was probably due to the fact that all of the acid in A was used up in neutralizing part of the NH_3, after which the NH_3 passed on to tube B, where it made the solution alkaline, under which condition AgCN does not ppt. Hence, it was found necessary to make the H_2SO_4 up about 6N in order to absorb all of the NH_3 in a run of about one to one and one half hour's duration. A concentration of N/20 was found to

be satisfactory for the $AgNO_3$ solution and one of N/10 for the NaOH.

The temperature of the carbon for the runs was varied from 425 degrees C to a maximum of 725 degrees, and the effects on the yield of HCN of running the NH_3 through the combustion tube faster and of diluting with illuminating gas were also tried. The results tabulated above all appear reasonable except the percentage yield of HCN in run #7. In this case it is probable that the high temperature used caused a partial decomposition of the NH_3 as well as a greater reaction with the active carbon to form HCN. The N_2 produced from such a partial decomposition would not be measured by the apparatus used, and hence the amount of total N_2 indicated is probably low. On the basis of the previous amounts of HCN obtained, the amount resulting from this run is about an average of fifteen times as large for the same length of time and rate of bubbling. Hence, the correct percentage of HCN is probably somewhat lower than 9.325 and would probably fall in the region of about 7-8%. Ordinarily there is practically no decomposition of NH_3 at any temperature below 650-700 degrees C, and hence the above effect does enter into the other results, although there is a possibility that the active C might lower this enough to cause slight decomposition of the NH_3 at 500-600 degrees C.

From the tabulated results, it appears that the

the process which occurs in the reaction zone tends to be a balance between the action of C on NH_3 to give HCN and the decompositions of this HCN and of NH_3. Any conditions which tend to remove the products of the first reaction (to form HCN) as soon as it is formed (such as dilution with illuminating gas and increased rate of passing the NH_3 over the carbon) increase the yield of HCN by tending to get it out of the reaction zone before the decomposition reaction has had a chance to get very far. The effect of cooling the gases by wrapping a wet towel around the exit tube from the reaction zone to the first absorption tube was also tried, and it was found that this also increased the HCN yield by cooling the gas below its decomposition temperature.

IV - SUMMARY

1 - In general, the same results were found for the reaction of NH_3 and active carbon as were determined for NH_3 and wood charcoal by Voerkelius, but the active carbon causes slight yields at temperatures below 700 degrees C, and seems to have the added effect of causing larger yields above 700 deg. than wood charcoal.

2 - No cyanogen is formed in the reaction, which tends towards being a balance between the formation of HCN and the decomposition of NH_3 and HCN. Methods of checking the decompositions by removing the HCN as fast as it is formmarkedly increase the yields of HCN.