THESIS.

The Equilibrium in a Process for the Production of Sodium Cyanide.

By

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The Equilibrium in a Process for the Production of Sodium Cyanide.

The normally large demand for supplies of the various nitrogenous products of the industries has been greatly increased as a result of the war. The importation of nitrates to the United States from Chile would be stopped in case of a naval blockade. The problem of assuring an adequate supply of such materials is, therefore, a very pertinent one. This may best be solved by the improvement of the present commercial processes for the fixation of atmospheric nitrogen and by the development of new processes, not at present successful commercially. Apparently, the most promising known process of the latter class ia based upon the formation of sodium cyanide by passing nitrogen gas over a mixture of sodium carbonate and carbon in the presence of a suitable catalyzer at high temperatures.

As will be shown later, cyanides readily undergo a reaction resulting in the formation of ammonia; this fact is of great importance, because with the increasing efficiency of the processes for oxidizing ammonia to nitric acid, a means is provided whereby the cyanides can be transformed into nitrates. The demand for nitrates can hardly be exaggerated for they form the base for practically all high explosives and are of great use as fertilizers. Sodium cyanide is of special importance to the Pacific coast as it forms the active agent in the cyanide process for gold recovery and is used most extensively in ridding the citrus trees of scale, thru fumigation. It is also largely used in electroplating.

The work described in this paper hinges on a reaction discovered in 1839 in the attempt of Lewis Thompson[1] to improve on the process then in use for the production of "Prussian blue". In recording this work he says:

> "Reflecting on these circumstances, it occurred to me that the atmosphere might be made to furnish, in a very economical manner, the requisite nitrogen, if allowed to act on a mixture of carbon and potash under favorable circumstances. The experiment proved on trial to be correct, and in a measure exceeded my expectations, for the carbonaceous matter is even improved by each operation. I found it necessary to use iron, for a reason which will be apparent in the explanation of this process; when iron is not employed a much higher temperature is required."

Soon after the publication of this article, many investigators commenced active work along the lines suggested by Thompson. Chief among these were Berzelius[2], Erdmann and Marchland[3], Formes and Young[4], Langlois[5], Rieken[6], Delbrück[7], and Bunsen and Playfair[8]. After many long investigations and controversies, they concluded that the alkali cyanides could be prepared as suggested by Thompson, but that the process was both uncertain and attended with very great difficulties and that no favorable conditions for their preparation in this manner were known.

In 1840, Newton[9] was granted a patent on a process for forming cyanides from the nitrogen of the atmosphere. At this time, the cyanides of the alkali metals were of little importance in their use as cyanides, but were used to make the ferrocyanides. Newton's process was very simple; air was forced thru retorts filled with potassium carbonate and charcoal. This process, altho worked commercially for some five or six years, was not practical and finally failed, chiefly due to the fact that very high temperatures were required; for Newton took no notice of Thompson's process, other than the general reaction, and left out the iron, thus using no catalytic agent, whatever.

Many other investigators have worked on this process but almost all of them have either disregarded the idea of using a suitable catalyzer, or have come to the conclusion that iron did not aid in the process.

In 1913, Bucher[11] demonstrated conclusively that the presence of a catalyzer such as iron or nickel intimately mixed with the mass of carbon and carbonate, was necessary if the reaction forming the cyanide was to go on with anything like an efficient yield at reasonably low temperatures.

Bucher took out many patents which were assigned to the Nitrogen Products Company, and several plants have been established. The success of these plants has been, however, of an indifferent nature. The apparatus used consists of an electrical furnace of the vertical type, heated by passing a current thru the resistor, which is uaually the charge itself. The charge, which is made up of coke and soda ash made into the form of briquets, is fed into the furnace at the top, while the nitrogen gas is forced up thru the bottom. The iron walls of the furnace act as the catalytic agent and the working temperature of the furnace is kept around 900° C. By use of oxygen-free nitrogen, oxidation of the iron parts of the furnace was avoided entirely in the electrical furnace and it was found to take place but slightly in an oil-burning furnace. In one type of furnace, producer gas was used instead of nitrogen.

The sodium cyanide formed in the briquets was removed by lixiviation or distillation <u>in vacuo</u>. The former process is more practical, because it does not necessitate the expensive machinery and operations used in vacuum distillations. However, in the lixiviating process a great many difficulties are encountered, chiefly due to the great tendency of the cyanide to change to ferrocyanide in the presence of iron; this takes place rapidily in hot water according to the following reaction,

$$6NaCN + Fe + 2H_2O = Na_4\,Fe\,C_6\,N_6 + 2\,NaOH + H_2\,.$$

Furthermore, a glance at the solubility curve shown in figure 1, shows that at temperatures below 35° C., the cyanide would take up water to form the dihydrate ($NaCN \cdot 2H_2O$) and hence the briquets would set into a solid mass. Therefore, the briquets should be lixiviated at a temperature slightly above 35°C., and the process carried on rapidily, lest hydrolysis of the cyanide take place, after either of the following reactions,

$$NaCN + 2\,H_2O \rightleftharpoons NH_3 + NaCOOH$$

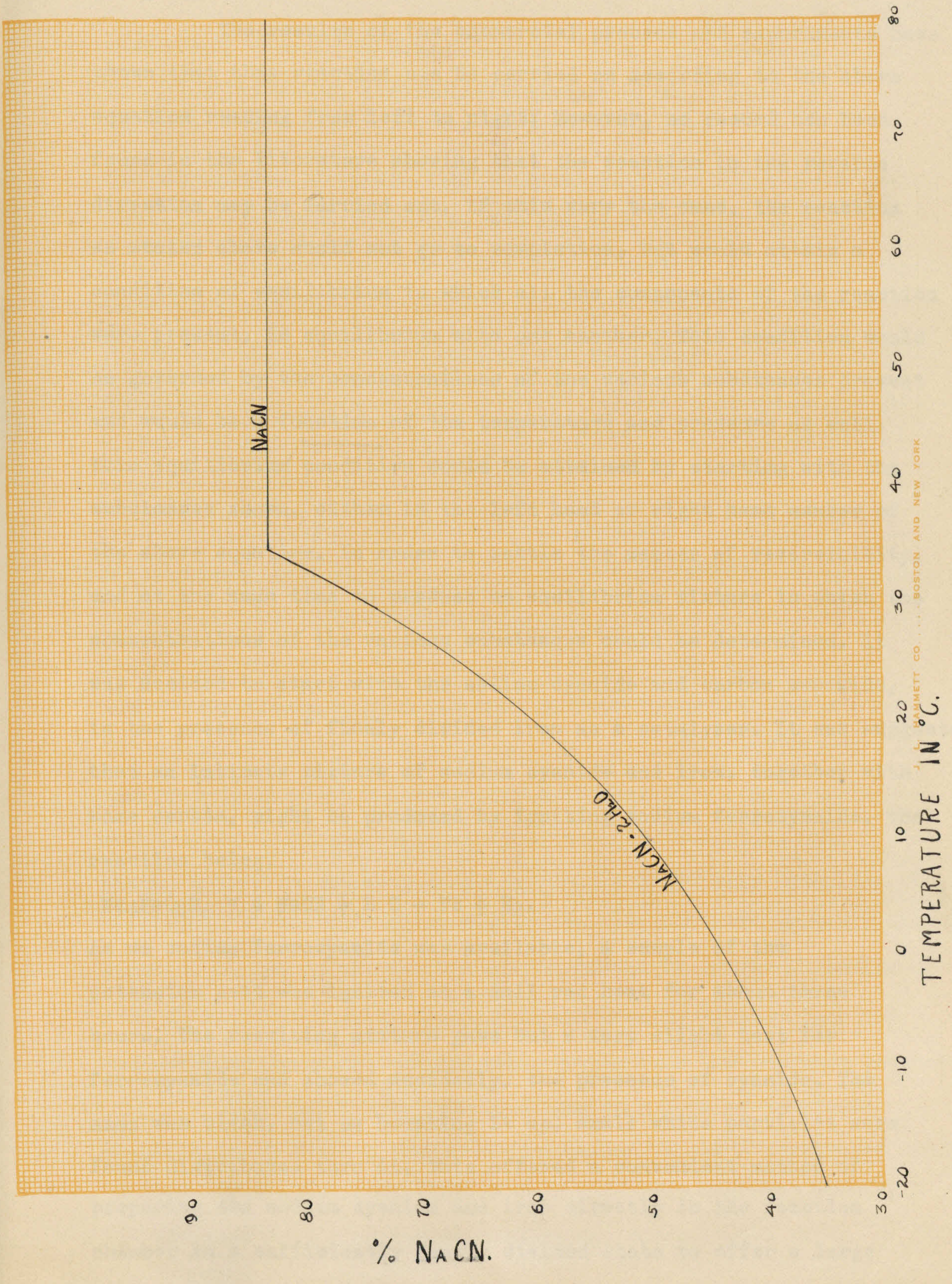
or

$$NaCN + 2\,H_2O \rightleftharpoons NaOH + HCN\,.$$

The latter reaction may be prevented to a large extent thru the addition of caustic soda, which decreases the concentration of the hydrogen ion, causing the reaction to go on in the opposite direction, when any hydrocyanic acid is present or formed. The hydrolytic reaction whereby sodium formate is formed, takes place only very slowly at temperatures under that of the boiling point of the solution; hence, caustic soda added to the lixiviating mass serves not only to prevent the formation of hydrocyanic acid thru hydrolysis, but also to raise the boiling point and, by salting out the sodium formate, to greatly increase the rate at which the first reaction goes on at a time when the ammonia is wanted.

The process appeared very promising and capable of further development to several members of the National Research Council and it was therefore thot advisable to investigate the equilibrium conditions of the reaction. The reaction involved in the

Figure 1.


NaCN
NaCN·2H₂O
TEMPERATURE IN °C.
-20
-10
0
10
20
30
40
50
60
70
80
% NaCN.
30
40
50
60
70
80
90

process is as follows,

$Na_2CO_3 + 4\ C + N_2 = 2\ NaCN + 3\ CO - 138500$ calories.

The results of the commercial process and experiments have shown that this reaction can be carried on according to the above equation reading from left to right; however, no record has been found in the literature showing that the reaction in the reverse direction may be carried out. If this were the case, the reaction as stated above would not go to completion, but would attain a condition of equilibrium in which all the components of the reaction were present, in equilibrium with one another. This condition would be governed by the concentrations of the various substances present and would be a function of the temperature and pressure as well. This equilibrium condition could be attained by starting with the substances shown, either in the left hand or right hand member of the above equation. In order to settle the matter of reversibility, and at the same time to produce an equilibrium mixture in which the concentrations of the various substances could be determined, it was decided to start with the sodium cyanide and carbon monoxide, in the presence of finely divided iron as a catalyzer. It was suggested that an intimate mixture of sodium cyanide and iron, together with some carbon, might be produced by igniting sodium ferrocyanide, the reaction being,

$Na_4FeC_6N_6 = 4\ NaCN + 2\ C + Fe + N_2.$

As no sodium ferrocyanide was available, a sample of the potassium salt was ignited at a dull red heat for about three hours. The resulting mixture gave but a very slight test for ferrocyanide and showed decidedly, the presence of cyanide. The mass was black, but on breaking it up, small white particles were found distributed thru it. This offered a convenient method of preparing the sodium cyanide and iron directly in the reaction chamber in a sufficiently finely divided state to offer a large reacting surface to the action of the carbon monaxide gas.

The necessary sodium ferrocyanide was prepared by boiling commercial " insoluble Prussian blue " with a concentrated solution of sodium hydroxide, the reaction being,

$Fe_4(FeC_6N_6)_3 + 12\ NaOH = 3\ Na_4FeC_6N_6 + 4\ Fe(OH)_3$.

The precipitate of ferric hydroxide was filtered off and the sodium ferrocyanide crystallized from the solution by evaporation.

In order that the ignited mass might be evenly distributed over a large surface, steel wool was highly compressed into "biscuits" which would fit snugly into the reaction chamber later described. They were allowed to absorb a saturated solution of the sodium ferrocyanide and then dried at 110°C., preparatory to charging into the reaction chamber.

The carbon monoxide gas was prepared by treating oxalic acid crystals with concentrated sulfuric acid. This reaction produces equal quantities of carbon monoxide and carbon dioxide, and the latter was removed by passing the gas thru an absorption train containing concentrated potassium hydroxide solution. The gas was drawn into a nine-liter bottle used as a gasometer and stored over air-free water which had been previously distilled. So perfect was the absorption of the carbon dioxide, that the resulting gas showed but fifty two hundredths of one per cent carbon dioxide. The apparatus for the generating and storing of the carbon monoxide is shown in figure 2. The large flask to the right of the gasometer is used to boil the distilled water before passing it over into the gasometer to force the carbon monoxide gas into the reaction chamber.

The reaction chamber consists of a bomb of two-inch seamless steel tubing, ten inches in length, a cross section of which is shown in figure 3. The joints were made by autogenous welding and the ends were provided with inlet and outlet tubes of

Figure 2.

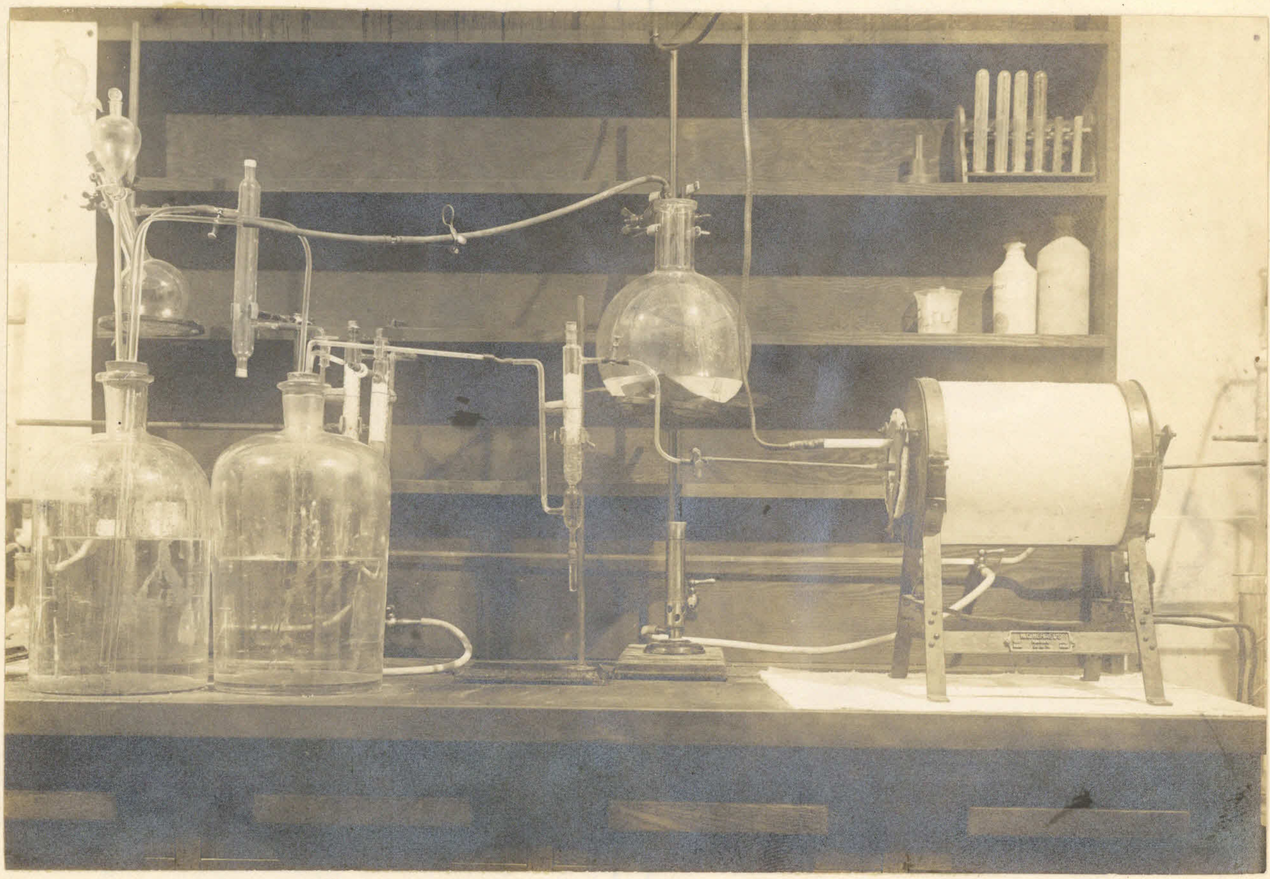
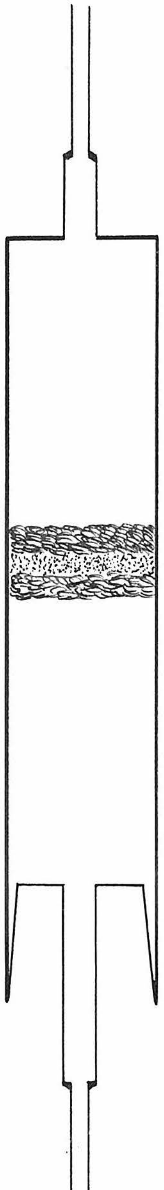


Figure 3.



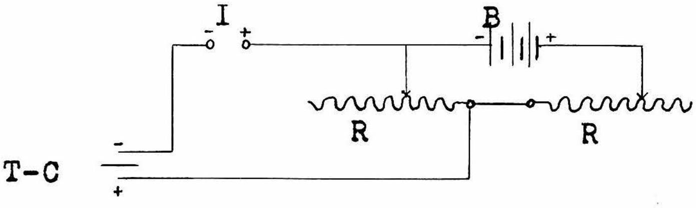
three-eighths-inch tubing which was welded into eighth-inch tubing. The right hand end of the bomb was shaped so that by grinding the joint on a carborundum wheel, the bomb was easily opened and rewelded for another run.

This reaction chamber or bomb was heated by an Heraeus electric furnace, wound with platinum ribbon as a resistor, and is shown in both figures 2 and 5. The temperature was controlled by regulating the voltage with an auto-transformer. The temperature measurements were obtained by the use of an iron-constanten thermocouple, in a quartz tube, using a Leeds and Northrup potentiometer indicator. As the base metal couple used gave a larger potential difference at high temperatures than could be measured on the indicator, a subsiduary circuit, shown in figure 4, was thrown in for temperatures over 780° C. This set up a counter electromotive force which was measured before being thrown in, and this measured amount was added to the indicator reading to give the correct potential difference on the thermo-couple. Very good temperature control was obtained and it was found that the furnace could be accurately kept at a constant temperature.

About four inches of the ferrocyanide "biscuits" were charged into the bomb and its open end welded to the inlet plate. It was then carefully tested for leaks by complete evacuation and was placed in the furnace and evacuated, after which the current was turned on.

As can be seen by the reaction, during the decomposition of the ferrocyanide, nitrogen would be evolved, and the cessation of this evolution of gas could be used as an indicator that the reaction was complete. This proved correct and during the ignition of the ferrocyanide the evolution of gases from the bomb gradually ceased. At about 250° C., about thirteen cubic centimeters of water were given off, due to the water of hydration contained in the ferro-

Figure 4.



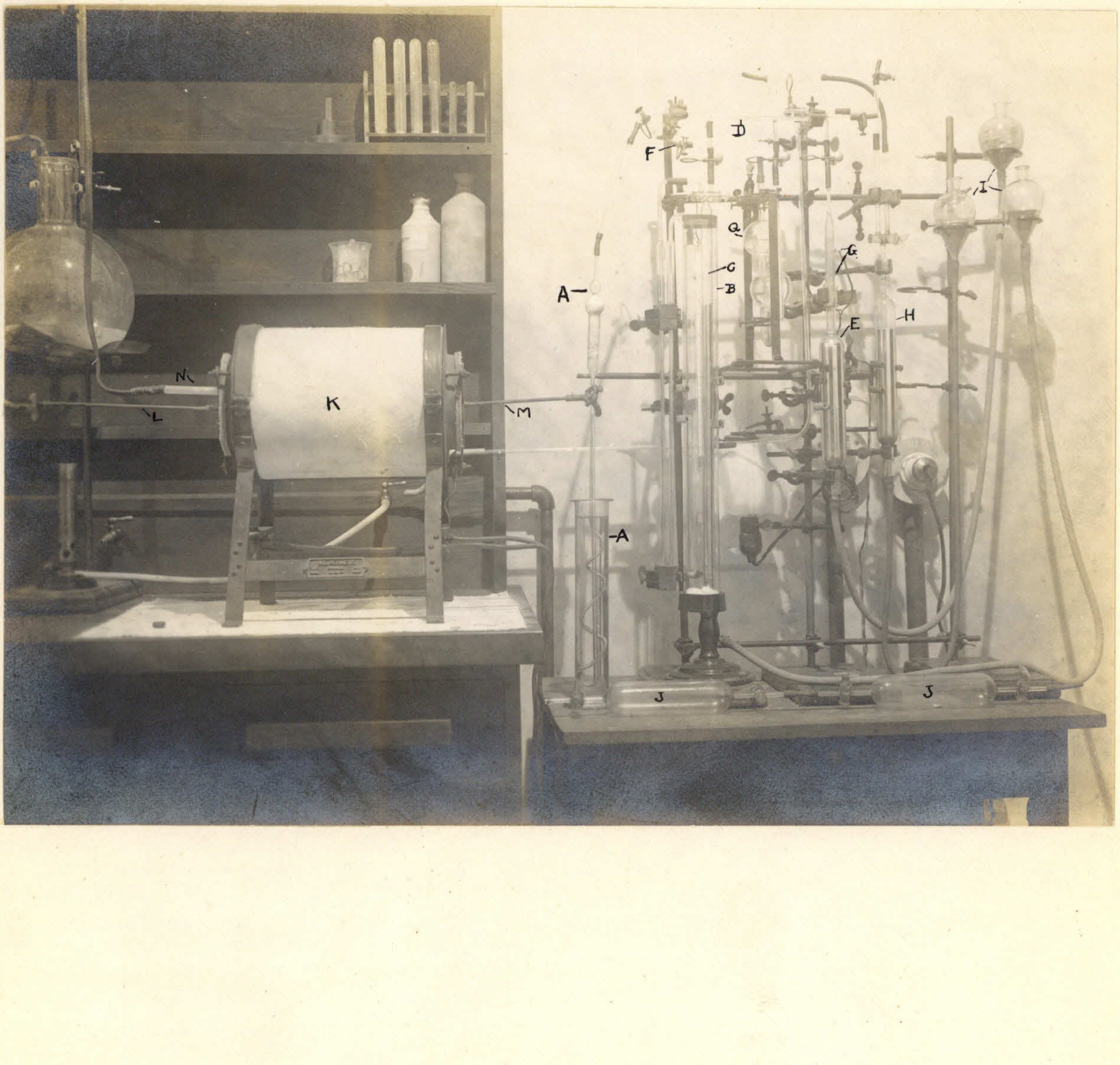
R	Dial Resistance Boxes.
B	Batteries.
I	Potentiometer Indicator.
T-C	Thermo-couple.

cyanide, Following this, gases were evolved at the rate of over one hundred cubic centimeters per minute. After several hours of heating, this rate of evolution had dwindled to less than two cubic centimeters per minute, and at this point the carbon monoxide gas was allowed to flow into the bomb slowly, previously flowing thru an absorption tower filled with concentrated sulfuric acid to remove any moisture in the gas.

Absorption of the carbon monoxide gas by the contents of the bomb was very marked, taking place even when the pressure in the bomb was considerably below atmospheric pressure. After about one and a half liters of carbon monoxide had been absorbed, the rate of absorption fell to two cubic centimeters per hour and equilibrium was thot to have been established. The temperature had been kept constant at 725° C. A sample of gas was then taken and the bomb cooled to 500° C., at which point, the temperature was held constant for several hours. A sample of the gas was taken here and the bomb removed and chilled by plunging into cold water.

The gases were sampled by passing thru a condenser and a calcium chloride tube, (A) of figure 5, to absorb any moisture present; they were then drawn into the gas analysis apparatus, shown in figure 5, where they were analyzed by the following procedure: Upon first entering the apparatus, the gas was allowed to come to the temperature of the burette jacket (B), after which it was measured in the burette (C). The gas was then forced thru the exhausted capillary tube (D), into a Hempel absorption pipette (Q), containing a concentrated solution of potassium hydroxide which absorbed any carbon dioxide present. It was then forced back into the burette and measured, whereupon it was passed into the explosion pipette (E) thru the capillary tube (D). A volume of oxygen corresponding to three quarters of the measured amount of the gas

Figure 5.



was then drawn into the burette thru (F), measured and forced slowly into the explosion pipette, ten cubic centimeters at a time. A platinum spiral at (G) was made to glow by means of an electric current and the gas was exploded or burned. After combustion was complete, the gas was again drawn into the burette, where it was allowed to come to temperature and was measured. It was then forced into the potassium hydroxide pipette where the carbon dioxide formed in the combustion was absorbed. The gas was then remeasured and the results of the analysis calculated.

In the figure, (H) is a mercury pump used in evacuating the apparatus and the bomb, and (I) are the mercury reservoirs used in forcing the gas thru the gas analysis apparatus. (J) shows two sample tubes used in taking samples of the gas. The furnace being at (K), the inlet and outlet tubes are shown at (L) and (M) respectively, while the pyrometer is at (N).

The bomb was opened as shown previously; the contents were removed and treated as follows: The steel wool which had matted together into a hard mass was leached out with two hundred cubic centimeters of water and aliquot parts analyzed. The results of this analysis were indefinite, due to the presence of some undecomposed ferrocyanide; however, a fairly large quantity of sodium carbonate was formed.

The results of the gas analysis are shown as follows:

A 1. Sample taken at 725° C.

Initial volume	41.54 c.c.
Oxygen added	33.12 c.c.
Total volume	74.66 c.c.
Volume after combustion	46.51 c.c.
Volume after absorption of CO_2	45.16 c.c.
Volume of CO_2	1.35 c.c.

Contraction 28.15 c.c.

CO_2 from contraction 0.68 c.c.

Excess contraction 27.47 c.c.

NH_3 = 4/5 of 27.47 = 22.01 c.c.

O_2 = 3/5 of 27.47 = 16.51 c.c.

N_2 formed = 2/5 of 27.47 = 11.01 c.c.

O_2 used = 0.68 + 16.51 = 17.19 c.c.

Excess O_2 = 32.12 - 17.19 = 15.93 c.c.

N_2 = 45.16 - 15.93 - 11.01 = 18.22 c.c.

CO = 1.35 c.c. = 3.25%

NH_3 = 22.01 c.c. = 52.99%

N_2 = 18.22 c.c. = 43.86%

Total 41.58 c.c. 100.10% Initial Volume 41.54 c.c.

Error 0.04 c.c. 0.10%

A 2. Sample taken at 500° C.

Initial volume 60.17 c.c.

Oxygen added 47.02 c.c.

Total volume 107.19 c.c.

Volume after combustion 93.10 c.c.

Volume after absorption of CO_2 91.50 c.c.

CO_2 1.60 c.c.

Contraction 14.09 c.c.

CO_2 from contraction 0.80 c.c.

Excess contraction 13.29 c.c.

NH_3 = 4/5 of 13.29 = 10.63 c.c.

O_2 = 3/5 of 13.29 = 7.97 c.c.

N_2 formed = 2/5 of 13.29 = 5.32 c.c.

O_2 used = 7.97 + 0.80 = 8.77 c.c.

Excess O_2 = 47.02 - 8.77 = 38.25 c.c.

N_2 = 91.50 - 38.25 - 5.32 = 47.93 c.c.

CO = 1.60 c.c. = 2.66%

NH_3 = 10.63 c.c. = 17.67%

N_2 = 47.93 c.c. = 79.66%

Total 60.17 c.c. h 99.99% Initial Volume 60.17 c.c.

Error = 0.01 c.c. = 0.01%

The close agreement and check obtained by the results more than justifies the calculation of the excess contraction as ammonia. The ammonia is undoubtedly due to the action of water upon sodium cyanide as shown in a reaction previously stated. The relatively large quantity of nitrogen as compared to the small amount of carbon monoxide shows that the reaction giving rise to the formation of sodium carbonate and nitrogen,is reversible.

Some tests were made on the residue from the leaching and these showed that some other compound other than the ones accounted for was present. This was also indicated by the large amount of carbon monoxide gas absorbed,over that required in the reaction. This compound was probably one of the formula, $Na_3FeC_5N_5 \cdot CO$, the corresponding potassium salt being formed almost quantitatively under similar conditions, according to Abegg[12].

The results of this experiment were considered encouraging, so it was thot best to repeat it using sodium cyanide in place of the sodium ferrocyanide which introduced needless complications. To this end, a small layer of compressed steel wool was placed in the center of the bomb so as to fit snugly enough to prevent the charge moving during the operation. Next to this was placed a thin layer of iron and sodium cyanide, intimately ground together. Another layer of compressed steel wool was then put in to keep this charge in place and yet porous to gases. Figure 3 shows a cross section of the bomb and this charge. The bomb was then rewelded, tested and placed in the furnace. After evacuating, the furnace was started and the determinations carried on as in the previous experiment, excepting that a pipette containing concentrated sulfuric acid was added to the gas analysis apparatus, to provide for the absorption of any ammonia in the gas.

Only a small quantity of carbon monoxide gas was absorbed, thus demonstrating that the addition product, $Na_3FeC_5N_5 \cdot CO$ had been formed in the previous experiment. The run of the furnace was about eight hours for the first sample and this was taken off at 900° C. The furnace was then cooled to 680° C., and run for three hours longer, when another sample was taken and the bomb removed and chilled with cold water.

The gases were analyzed with the following results:

B 5 a. Sample taken at 900° C.

Initial volume	53.46 c.c.		
After absorption of CO_2	52.13 c.c.	Original CO_2	1.33 c.c.
Oxygen added	42.88 c.c.		
Total volume	95.01 c.c.		
After combustion	74.73 c.c.	Contraction	20.28 c.c.
After absorption of CO_2	48.47 c.c.	CO_2 formed	26.26 c.c.
Contraction from CO_2	13.13 c.c.	Excess contraction	7.15 c.c.

Oxygen used = 3/5 of 7.15 = 4.29 c.c.

NH_3 = 4/5 of 7.15 = 5.72 c.c.

N_2 = 2/5 of 7.15 = 2.86 c.c.

Total O_2 used = 4.29 + 13.13 = 17.42 c.c.

Excess O_2 = 42.88 - 17.42 = 25.46 c.c.

Residual gas = 48.47 - 25.46 = 23.01 c.c.

N_2 in original gas = 23.01 - 2.86 = 20.15 c.c.

N_2 = 20.15 c.c. = 37.69%

CO_2 = 1.33 c.c. = 2.49%

CO = 26.26 c.c. = 49.12%

NH_3 = 5.72 c.c. = 10.70%

Total 53.46 c.c. 100.00% Initial volume 53.46 c.c.

Error 0.00 c.c. = 0.00%

B 5 b. Sample taken at 680° C. Combustion run on original gas.

Initial volume 54.62 c.c.

After absorption of CO_2 49.10 c.c. CO_2 in original gas 5.52 c.c.

After combustion 48.81 c.c. Contraction 0.29 c.c.

After absorption of CO_2 48.53 c.c. CO_2 formed 0.28 c.c.

Contraction from CO_2 0.14 c.c. Excess contraction 0.15 c.c.

NH_3 = 4/5 of 0.15 = 0.12 c.c.

O_2 = 3/5 of 0.15 = 0.09 c.c. O_2 used by CO 0.14 c.c.

N_2 formed = 2/5 of 0.15 = 0.06 c.c.

Total O_2 used = 0.14 + 0.09 = 0.23 c.c. = O_2 in the original gas.

CO used in combustion 0.28 c.c.

NH_3 used in combustion 0.12 c.c.

N_2 formed in combustion 0.14 c.c.

Second combustion.

Volume from first combustion 48.53 c.c.

Oxygen added 36.93 c.c.

Total volume 85.46 c.c.

After combustion 76.52 c.c. Contraction 8.94 c.c.

After absorption of CO_2 63.07 c.c. CO_2 formed 13.45 c.c.

Contraction from CO_2 6.72 c.c. Excess contraction 2.22 c.c.

NH_3 = 4/5 of 2.22= 1.78 c.c. 02 = 3/5 of 2.22 = 1.33 c.c.

N_2 formed = 2/5 of 2.22= 0.89 c.c. O_2 used = 1.33 + 6.72 = 8.05 c.c.

Excess O_2 = 36.93 - 8.05 = 28.88 c.c. Residual gas 63.07 c.c.

N_2 = 63.07 - 0.89 - 28.88 = 33.30 c.c.

CO = 13.45 + 0.28 = 13.73 c.c. = 25.14%

CO_2 = 5.52 c.c. = 10.10%

NH_3 = 1.78 + 0.12 = 1.90 c.c. = 3.48%

N_2 = 33.30 c.c. = 60.97%

O_2 = 0.23 c.c. = 0.42% Total 100.11%

Total 54.68 c.c. Initial volume 54.62 c.c.

Error 0.06 c.c. = 0.10%

The bomb was then opened and the charge was found apparently unchanged except that it was cemented together into a porous disk. A sample of this was removed and dissolved in one hundred and fifty cubic centimeters of water at 50° C. Aliquot parts of fifty cubic centimeters each were analyzed by titrating with tenth normal solutions of silver nitrate and nitric acid, using methyl orange as the indicator with the latter reagent. The results of the analysis showed the ratio of cyanide to carbonate to be 0.11 to 89.81 or 0.01225, while the analysis of the cyanide used showed it to be 98.53 to 3.38 or 29.1657.

In all probability, a liquid phase was present, being a saturated solution of sodium carbonate in molten sodium cyanide. In this case equilibrium would depend upon the pressure of the nitrogen and carbon monoxide gases in the reaction chamber.

The experiments show that the reaction is reversible, and that the equilibrium is at a point at which the sodium carbonate content of the mixture is very high in proportion to the cyanide. In order to make the process commercially successful, the necessity is shown for pushing the reaction as far as possible from equilibrium, by passing a rapid stream of nitrogen thru the apparatus in order to force out the carbon monoxide formed.

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