THESIS

EQUILIBRIA INVESTIGATION OF THE BUCHER PROCESS FOR NITROGEN FIXATION.

By

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EQUILIBRIA INVESTIGATION OF THE BUCHER PROCESS FOR NITROGEN FIXATION.

The purpose of this investigation was to obtain data which would aid in increasing the efficiency of the Bucher process for the production of sodium cyanide. The indications are that this process when perfected will compete favorably with other processes for the fixation of atmospheric nitrogen, by furnishing ammonia products with a minimum outlay for apparatus, labor and raw materials.

The historical development of the process, which dates from approximately 1840, has been completely outlined by Bucher (1). During the period of development, however, very little work has been done upon the equilibrium conditions of the reactions involved; hence the process has not been developed to its fullest extent.

<u>Essentials of the reaction.</u>

The fundamental reaction of the process is $NA_2CO_3 + N_2 + 4C \rightleftarrows 2\ NACN + 3CO - 138,500$ cal. (1).

The presence of a catalyzer such as iron or nickel is required if an appreciable yield of sodium cyanide is to be obtained in a reasonable time. That the reaction is reversible has already been proven; the equilibrium point is far to the carbonate side of the reaction at temperatures near 850° C. The commercial operation of the process has been considered in detail by Bucher (1); only cut and try methods of control, however, have been used in his development.

The large heat content change (-138,500 cal.) of the reaction indicates that the equilibrium constant changes rapidly with the temperature. It was therefore thought probable that an accurate determination of the equilibrium constant at various temperatures would lead to a knowledge of the most favorable temperature for the commercial operation of the process, and the present thesis describes the attempt to obtain this information.

In this work the equilibrium constant K of the reaction was determined over the temperature range 898° to 1016° C. This constant is the ratio of the cube of the partial pressure of carbon monoxide over the reacting mixture, to the partial pressure of nitrogen over the mixture for a given composition of gas admitted to the reaction chamber. The greater the value of K the greater is the tendency of the reaction to go toward the production of sodium cyanide. The experiments described below show that the value of K increases very rapidly with the temperature, and indicate that as high a temperature should be used in commercial operation of the Bucher process as is consistent with commercial limitations.

Experimental.

The bomb

The reaction chamber, or bomb, as it will hereafter be called, is shown at A, Fig I. It consisted of a short piece of seamless steel tubing about 2-1/4" in diameter, and varying in length from 4 to 9 ", the ends being closed by plates into which tubes for the entering and exit gases were autogenously welded.

After welding on one of the end plates the joints were tested for leaks, a thin layer of steel wool was placed on the bottom of the tube and the charge inserted. Another layer of the wool was then placed over the charge and the other end plate welded in place. The entire bomb was then tested for leaks. In the later experiments the thermocouple tube was placed within the

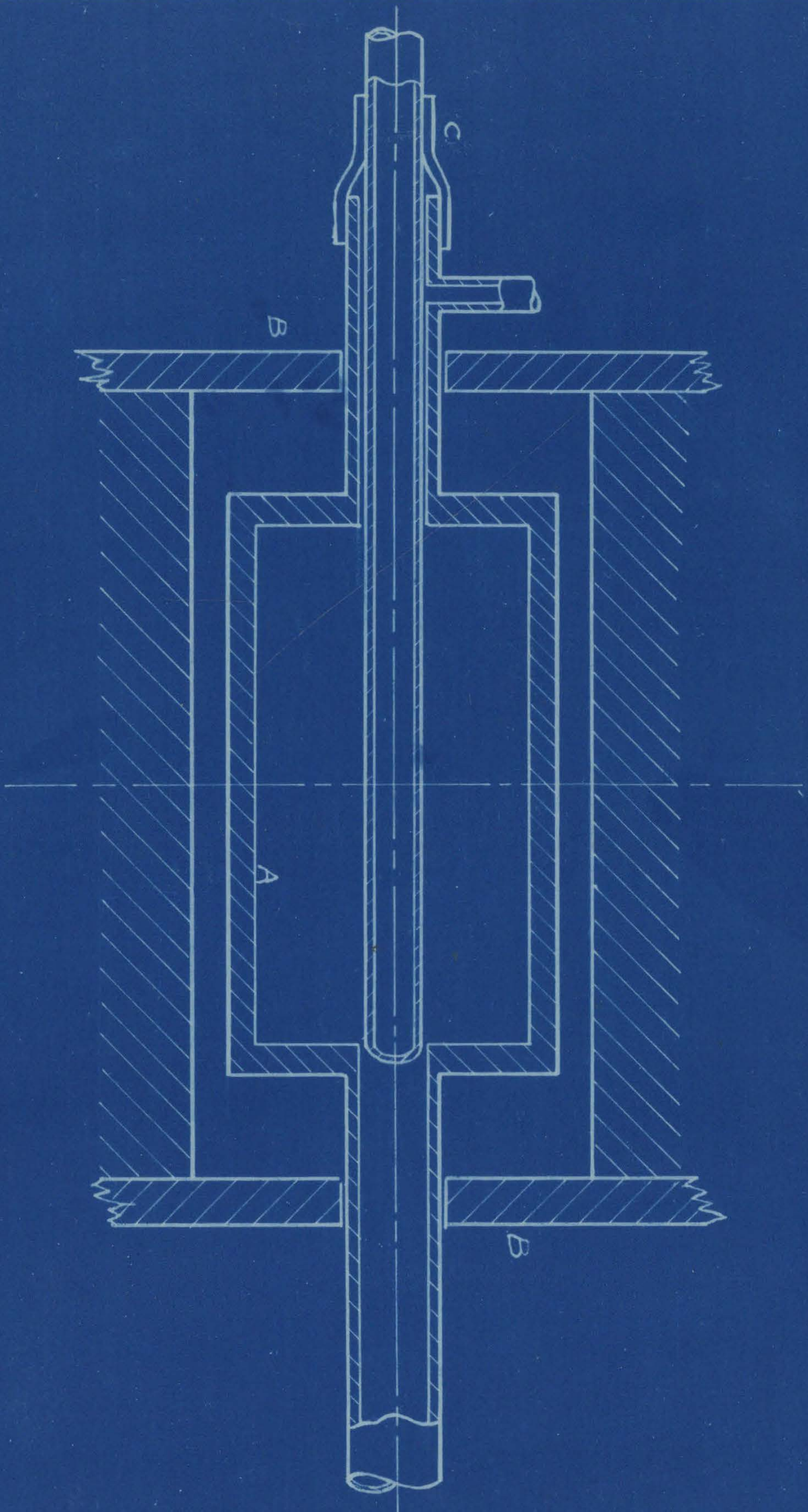

FIGURE I

gas entrance tube, which made it necessary to charge the bomb with this tube in place, to prevent difficulty in getting the tube into the bomb.

The steel tubing served well as a reaction chamber, although the length of the run was limited to the time necessary for the tube to oxidize through and develop leaks. In only one case, however, did this factor make any material difference in the results obtained.

Furnace

A Heraeus platinum-wound electric furnace was used to heat the bomb, variations in temperature were obtained by means of a transformer which was capable of giving voltages in steps of 0.5 from 0 to 110. The first two or three runs were made using only asbestos boards to prevent radiation from the open ends of the furnace chanber. In these runs the temperature was measured by means of a thermocouple placed between the interior furnace wall and the bomb, moving the tip of the couple from one end of the tube to the other showed a large variation in temperature. Since it was known that a small variation in temperature caused a large change in the equilibrium constant at temperatures near 1000°C, it became evident that a much more uniform heating of the bomb would be necessary. To avoid unnecessary radiation at BB, Fig I, end plug containing heating coils were used, thus supplying heat to balance that lost by radiation. To make the construction of these plugs simple and at the same time to determine with more accuracy the true temperature of the charge, the thermocouple was inserted in the bomb through the gas entrance tube, the joint between the couple tube and gas entrance tube being made tight by means of the rubber tube C. With this arrangement it was necessary to have only one hole in each end plug. The details of construction of the plug are shown in the assembled drawing Fig. II. They were made according to the general principles outlined in the Bulletin of the Bureau of Standards (3), having alternate layers of heat conducting and heat insulating materials so arranged that the conduction was perpendicular to the path of radiation, thus tending to transfer the heat to the furnace walls rather than to the air. At the outside end of the plug a variable source of heat was applied, thus theoretically enabling the radiation loss to be counteracted at any temperature. Nichrome wire, protected by a layer of alundum cement, was used as the heating element and a flange of asbestos was placed outside the nichrome wire to insure the complete covering of the open ends of the furnace chamber.

With the plugs in place, during a run, the temperature gradient inside the bomb was obtained by moving the tip of the thermocouple from one end of the bomb to the other by one centimeter steps, and reading the corresponding temperature by means of a potentiometer indicator. These data enabled curves to be plotted showing the temperature of various parts of the charge. The temperature variation in the central part of the bomb was small, not exceeding 6 or 7°C, when a potential difference of 35 volts was used across the end plugs. The difference in temperature between a few centimeters at the ends of the bomb and the center of the bomb was much larger, often amounting to about 15°C. Since the steel wool occupied some space at the ends, it is probable that the variation in the charge itself was not over 6 or 7°C.

Temperature measurement

The thermocouple first used was of iron and constantan. This combination did not prove satisfactory for temperatures over 900°C, consequently a couple of platinum and platinum- 1070 rhodium was used for temperatures above this point. The calibration curve supplied with the couple was used rather than a calibration made in the laboratory.

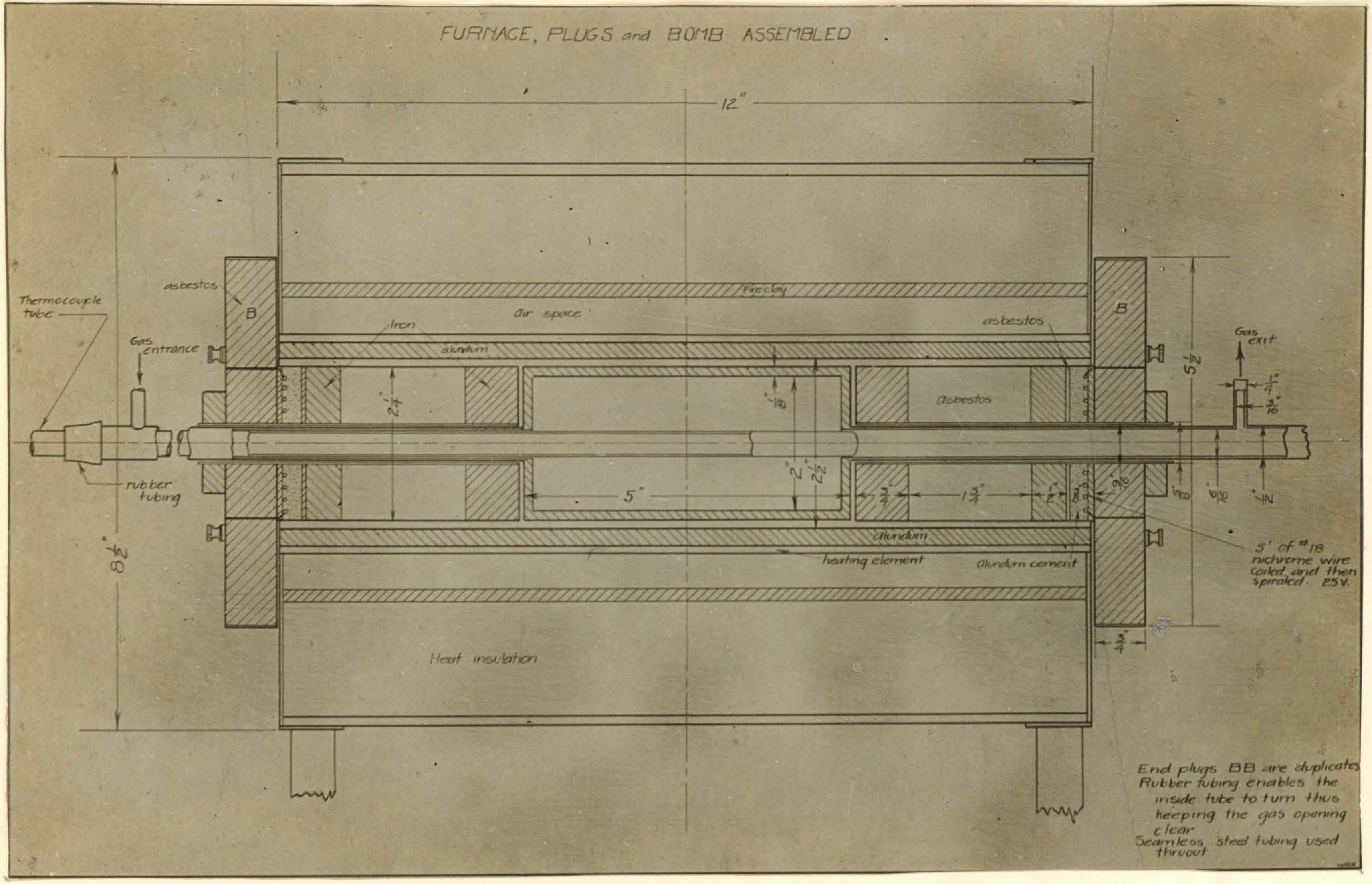
FURNACE, PLUGS and BOMB ASSEMBLED
12"
8½"
5½"
Thermocouple tube
Gas entrance
rubber tubing
asbestos
B
B
Fireclay
air space
Iron
alundum
asbestos
Asbestos
Gas exit
1/4"
3/16"
2¼"
1/8"
2"
2½"
5"
3/4"
1¾"
1/2"
9/16
1/2"
alundum
heating element
alundum cement
5' of #18
nichrome wire
coiled and then
spiraled. 25V.
3/4"
Heat insulation
End plugs BB are duplicates
Rubber tubing enables the
inside tube to turn thus
keeping the gas opening
clear
Seamless steel tubing used
thruout

Figure II

The wires were placed in quartz tubes enclosed in a piece of small seamless steel tubing; this tube was inserted into the bomb-thermocouple tube. A Leeds and Northrup potentiometer indicator # 36310 was used to measure the potential difference set up in the thermocouple.

Figure II is an assembled drawing of the bomb, furnace and end plugs as used in the later experiments; the various parts were constructed as indicated in the above discussion.

Gas Analysis

Since a knowledge of the composition of the gases in equilibrium with the solid materials is necessary to compute the equilibrium constant K, an accurate means of analyzing the equilibrium gas mixtures was necessary. Throughout the entire investigation the gas analysis apparatus gave trouble. A description of the several methods used and a typical calculation of data obtained by each are given below:

1. A combustion pipette containing an electrically heated platinum coil was first used for the determination of hydrogen and carbon monoxide, known quantities of oxygen being added to the gas mixture to enable combustion to take place. The gas was freed from moisture before each reading by causing it to pass through a calcium chloride tube. Carbon dioxide was determined by absorption in KOH solution, and excess oxygen by means of a phosphorus pipette. The residual gas was considered to be all nitrogen. The apparatus is shown diagrammatically in Fig. III.

In making an analysis the following procedure was used:

Before drawing a sample into the measuring burette A, the capillary tubes and header were evacuated. This was done by the aid of a two-way stop cock on the measuring burette, which allowed the burette to be used as a pump. Since

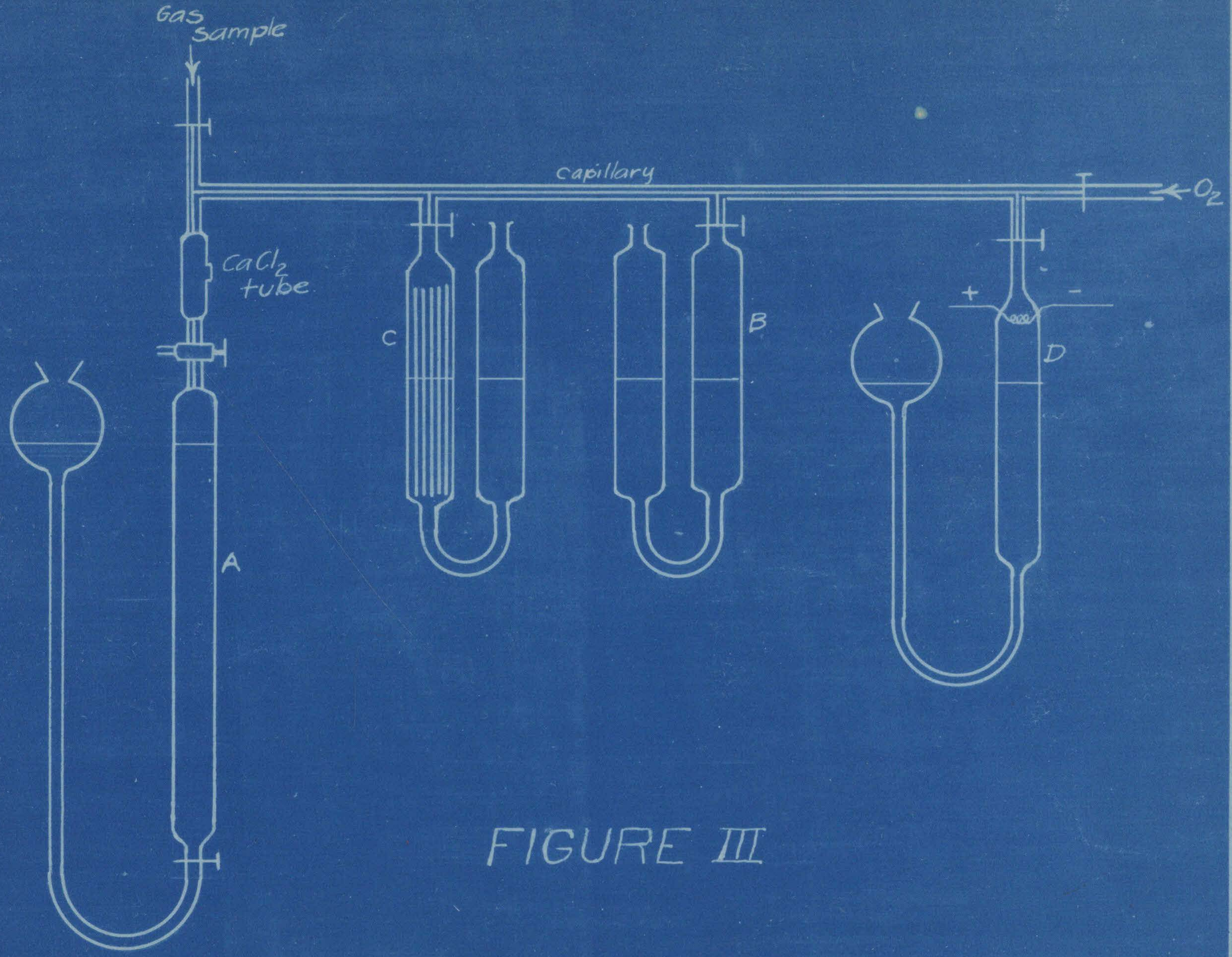

FIGURE III

ercury was used in the burette, a good vacuum could be obtained in this way. ir was then drawn into the burette and the volume read. When the stop cock was urned so that the evacuated capillary tubes were connected with the burette a ortion of the air rushed in to fill the evacuated space. The volume of air re- aining in the burette was then read. The difference between the readings gave he volume of the capillary. All the air was then again pumped out of the capil- ary, and the gas sample drawn in and measured. It was then treated successive- y with potassium hydroxide in Pipette B, phosphorus in pipette C, oxygen in he combustion tube D, potassium hydroxide in B, and again with phosphorus in C.

The analysis data and calculations for a typical sample are shown elow:

DATA SHEET

eading	Temp.	Press.	Vol.	Total Vol.	Stan. Vol.	Contraction.
urette	219	748.0	53.1			
ur & Capillary	21.9	748.0	50.2			
ol. of Capillary						2.6
nitial Vol.	22.4	748.0	69.7	72.1	65.7	
fter KOH	22.7	748.0	69.8	72.2	65.7	0.0
fter Phos.	22.8	748.0	68.3	70.7	64.2	0.5
ample O_2	21.9	777.0	100.0	102.4	97.0	
fter comb.	20.2	747.8	77.5	79.9	73.2	23.8
fter KOH	21.8	747.7	74.1	76.5	69.7	3.5
fter Phos.	22.1	748.0	49.8	52.2	47.6	21.9
urette	22.5	748.0	34.9	31.8		
ur.& Capillary	22.5	748.0	32.5	29.6		2.2

CALCULATIONS

The oxygen used was of the following composition:

N_2	1.39%
CO_2	2.31
O_2	96.32
	100.02%

a) Oxygen added = 97.0− 64.2 = 32.8 cc.
32.8 x .0139 = 0.5 cc of N_2
32.8 x .0231 = 0.8 cc of CO_2

b) CO forms CO_2 by combustion, therefore

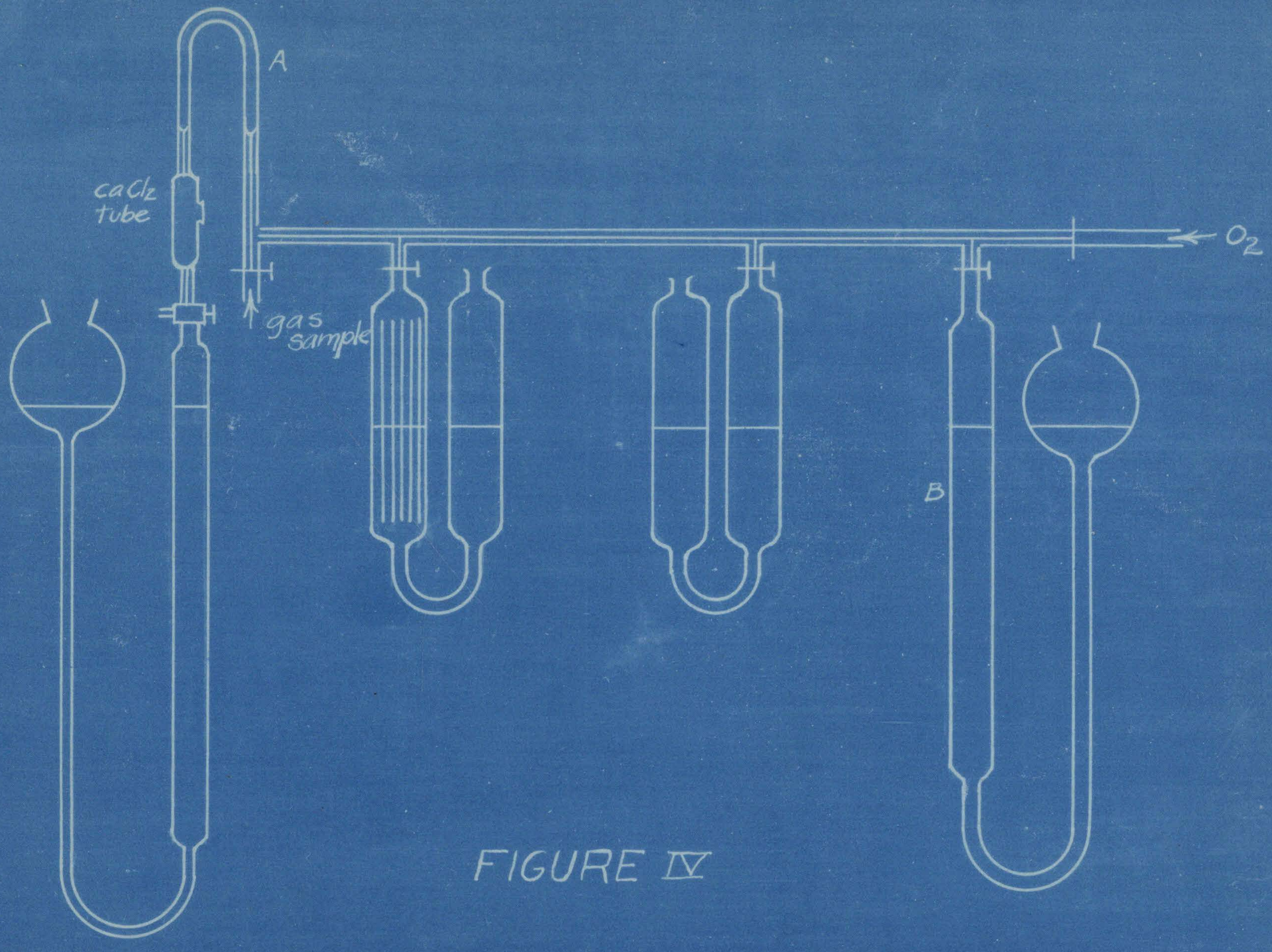

FIGURE IV

3.5 - 0.8 = 2.7 cc = no. of cc of CO originally present
since $2\ CO + O_2 \rightarrow 2\ CO_2$

(c) $\underline{N_2}$ 52.2 - 0.5 = 51.7 cc originally present.

(d) $\underline{H_2}$ was determined by excess contraction over that due to the burning of the CO present.

$$\begin{array}{lcr} \text{Total contraction after combustion} & = & 23.8\ \text{cc} \\ \text{Contraction due to CO} = 2.7/2 & = & \underline{1.4} \\ \text{excess contraction} & & 22.6\ \text{cc} \end{array}$$

The hydrogen originally present was then
22.6 x 2/3 = 15.1 cc since $2\ H_2 + O_2 \rightarrow 2\ H_2O$

Final results:

$$\begin{array}{rlrl} CO_2 & = 0.0\ \text{cc} & = & 0.0\ \% \\ O_2 & = 0.5\ \text{"} & = & 0.8 \\ CO & = 2.7\ \text{"} & = & 4.1 \\ M_2 & = 47.1\ \text{"} & = & 71.8 \\ H_2 & = \underline{15.1}\ \text{"} & = & \underline{23.0} \\ & \ 65.4\ \text{"} & & 99.7\% \end{array}$$

Use of the Ca CL_2 tube made the calculations of vapor tension unnecessary.

Analyses of the same sample made by the above method could not be made to consistently check with one another and the total percent varied from 94 to 106. This was probably due to oxidation of some of the nitrogen in the combination pipette.

2. In a second modification of the gas analysis apparatus, the combustion pipette was replaced by a tube containing powdered cupric oxide heated to 285° C after the manner described by Burrell and Oberfell (4). Potassium hydroxide and phosphorus pipettes were used as in the preceding method. The arrangement of the apparatus is shown in Fig. IV.

The oxidation of CO and H_2 was carried out in the CuO tube A. This tube was heated by means of a small electric furnace wound with advance wire and capable of attaining a temperature of 325° C on 25 volts. The cupric oxide was renewed, after being reduced, by passing oxygen slowly through the heated tube into the auxiliary pipette B and back again. In this type of apparatus the contraction in volume of the gas sample after passing over the heated cupric oxide was taken as a direct indication of the hydrogen present. The CO in the sample was burned to CO_2 without change of volume and was determined by absorbing, in KOH, the CO_2 formed.

A typical calculation from data obtained by this method is given in the following table:

DATA SHEET

Reading	Temp.	Press.	Vol.	Total Vol.	Stan. Vol.	Contraction.
Burette	21.6	748.6	42.2			
Bur. & Cap.	21.6	748.6	39.2			
Vol. of Cap.						3.0
Initial	21.6	748.9	50.1	53.1	48.5	
After KOH	21.6	748.9	50.1	53.1	48.5	0.0
" Phos.	21.6	749.0	50.0	53.0	48.4	0.1
" CuO	21.6	749.1	48.7	51.7	47.2	1.2
" KOH	21.6	749.1	5.3	8.3	7.6	39.6
" CuO	21.6	749.2	5.3	8.3	7.6	0.0
" KOH	21.6	749.2	4.4	7.4	6.8	0.8
Burette	21.6	749.2				
Bur. & Cap.	21.6	749.2				
Vol. of Cap.						3.0

Final Results:

CO_2 - 0.0. cc = 0.0 %
O_2 - 0.1 = 0.2
H_2 - 1.2 = 2.5
CO -39.6 + 0.8 = 83.3
N_2 - 6.8 = 14.0
48.5 cc 100.0 %

Analyses of samples of the same gas by this method gave varying results for the hydrogen and carbon monoxide content, the variation being as high as ten per cent in some cases. The total percent for each analysis, however, always came close to 100%. The analyses yielded suspiciously large amounts of hydrogen, and since the arrangement of the apparatus necessitated cooling the cupric oxide after passing the gas through and before reading the volume, it was thought possible that some carbon dioxide was absorbed by the cooled cupric oxide to form cupric carbonate. This absorbed CO_2 would appear in the calculated results as hydrogen, in the above method of analysis, and thus introduce considerable error.

Table I gives the results of analyses of the same gas sample by the oxygen combustion method and the cupric oxide method. The results are too irregular to be of use in an accurate determination of the equilibrium constant. Especially the percentage of carbon monoxide must be determined, as this value is cubed in the expression for the constant.

A gas sample of known composition was made and analyzed by the CuO method, but the results gave no better checks than the analyses shown in the table.

Other modifications of the apparatus consisted of the substitution of a pipette containing alkaline pyrogallol solution for the pipettes containing phosphorus and potassium hydroxide. This solution removed the oxygen and carbon dioxide at the same time, thus avoiding unnecessary operation.

The final apparatus was essentially that shown in Fig. IV with exception that the potassium hydroxide and phosphorus pipettes were replaced by one pipette containing alkaline pyrogallol. In future work the apparatus will be so arranged that the cupric oxide tube is kept hot at all times, the gases contained within it being drawn out by means of a mercury pump, and added to those in the measuring burette. The hot tube can then be cut off completely from the rest of the apparatus while the gas volume is being measured. It is hoped that this type of apparatus will eliminate any possibility of cool CuO absorbing CO_2. As it is, calculations based on the results obtained thus far can be only approximated and of use only in drawing general conclusions.

	Combustion tube using Oxygen gas.						Cupric Oxide tube			Combined app.
Sample	A	B	C	D	E	Aver.	A	B	Aver.	C.
% CO_2	7.3	7.7	7.9	8.2	6.7	7.6	6.5	5.5	6.0	3.98
" O_2	13.3	13.0	13.5	13.0	14.7	13.5	13.1	9.1	11.1	8.39
" CO	11.1	14.6	14.9	13.9	12.3	13.4	12.3	7.2	9.7	3.98
" H_2	15.4	13.7	13.9	12.6	9.9	13.1	54.2	62.7	58.5	66.67
" N_2	52.0	51.3	51.1	50.9	57.0	52.5	14.0	15.5	14.7	16.97
Total.	99.7	100.3	101.3	98.6	100.6	100.1	100.1	100.0	100.0	99.99

TABLE I

The charge

Preliminary work was begun upon the question of the reversibility of the reaction by first using a charge made up by igniting sodium ferrocyanide, the reaction being-

$$NA_4FE\ (CN)_6 \longrightarrow 4\ NACN + 2\ C + Fe + N_2$$

The cyanide, carbon and iron are formed by this process in intimate contact with one another, and should constitute a satisfactory charge for the bomb. Experience showed, however, that some other compound than cyanide was also formed from the ferrocyanide by ignition (2).

The charge used in the next few experiments consisted of iron, charcoal and sodium cyanide intimately ground together and placed in layers with plugs of steel wool separating them. Thus it was kept porous, intimately mixed and in such a condition that a large amount of surface was exposed. After heating and passing in carbon monoxide the charge was rapidly cooled and a portion of it tested for sodium carbonate. A large amount of this compound was found to be present. Since Bucher has shown that the reaction proceeds also in the opposite direction under proper conditions, the reversibility of the reaction is established. Analyses of the gas mixtures in equilibrium with the charge did not, however, give sufficient reliable data for a calaulation of the equilibrium constant K.

The charges used in experiments following the above have been of two types: (1) Sodium cyanide, sodium carbonate, iron and carbon in definite proportions were intimately ground together, and placed with separating plugs of steel wool in the reaction chamber;

(2) A mixture similar to the above was treated with a small amount of water and passed through a meat grinder, producing long pencils of the desired composition. These pencils were dried in an oven at 90 - 130 ° C for eight hours

and then transferred to a dessiccator until ready for use. Hydrolysis probably took place to some extent in accordance with the following reaction:

$$NACN + 2\ H_2O \rightleftarrows NAOH + HCN$$

rather than according to the reaction.

$$NACN + 2\ H_2O \rightleftarrows NH_3 + NACOOH$$

since the odor of ammonia could not be detected. A thin white coating was noticeable on the surface of the pencils. This coating was probably either cyanide or sodium hydroxide. In the event that it was the hydroxide, it is known that the relation of carbon monoxide to nitrogen in the equilibrium mixture would not be altered, since the only effect of the presence of sodium hydroxide would be the formation of hydrogen through reaction with the carbon monoxide.

Analysis of the Charge

In future work it will be desirable to analyze the charge both before and after the run. A method based on suggestions by Dr. Graham Edgar was tested and found satisfactory for the accuracy desired. In this method the sample to be analyzed, consisting essentially of a mixture of sodium carbonate, sodium cyanide and sodium hydroxide, with a possible small amount of sodium, is first treated with a small amount of water cooler than 30°C (to avoid the formation of $NA_4Fe(CN)_6$) in an evacuated flask which is connected to the gas analysis apparatus. Any sodium present will react with the water to form hydrogen, the volume of which is measured in the gas analysis apparatus. From this volume the amount of sodium originally present can be calculated.

The aqueous solution obtained after filtering off the iron and carbon is then treated with an excess of 0.5 N $Ba(NO_3)_2$ solution and filtered. It is best to perform the filtration under a bell jar containing air free from CO_2 and to wash the precipitate with freshly boiled water. This step precipitates all the carbonate as $BaCO_3$ according to the reaction:

$$Na_2CO_3 + Ba(NO_3)_2 \longrightarrow \underline{BaCO_3} \quad 2\ NaNO_3.$$

The solubility of $BaCO_3$ is 1.86 x 10^{-3} grs. in 100 grs. of solution at 16°C (5). Since large excess of water was avoided in the first step it is apparent that practically all the carbonate present will be precipitated.

The filtrate obtained from the $Ba(NO_3)_2$ treatment is diluted to 500 cc and a 50 cc sample titrated with a standard solution of 0.1 $NAgNO_3$ until a permanent turbidity is formed. This point is best observed by placing the container over a piece of black glazed paper. The burette is then read. The reaction which takes place results in the production of the soluble $NaAg(CN)_2$ according to the equation:

$$2\ NaCN + AgNO_3 \rightleftharpoons NaAg(CN)_2 + NaNO_3.$$

As soon as all the $(CN)^-$ ions are used up in producing $NaAg(CN)_2$ the following reaction takes place upon the addition of more $AgNO_3$.

$$NaAg(CN)_2 + AgNO_3 \longrightarrow 2\ \underline{AgCN} + NaNO_3$$

At this point the permanent turbidity appears.

AgCN is soluble to the extent of 2.2 x 10^{-5} grams per 100 grams of solution (5) . $NaAg(CN)_2$ in solution however produces fewer Ag^+ ions than AgCN in solution, consequently no AgCN will be precipitated until all the $(CN)^-$ ions present have reacted to form $NaAg(CN)_2$. As soon as this conversion is complete an excess of Ag^+ ions from the $AgNO_3$ will cause the precipitation of the AgCN. The amount of $AgNO_3$ required to produce the first sign of a precipitate of AgCN affords a basis for calculation of the amount of $(CN)^-$ originally present, one Ag^+ being equivalent to 2 $(CN)^-$.

All of the $NaAg(CN)_2$ is then converted into insoluble AgCN by adding an amount of $AgNO_3$ equal to the amount required to produce the first turbidity. Further addition of $AgNO_3$ causes the following reaction to take place:

$$2\ NaOH + 2\ AgNO_3 \rightarrow \underline{Ag_2O} + NaNO_3 + H_2O.$$

Enough $AgNO_3$ is added to insure the complete precipitation of the hydroxide as the brown Ag_2O. This compound is soluble to the extent of 2.15×10^{-3} grs. in 100 grs. of solution (5) and is consequently practically all precipitated.

The solution containing the precipitated Ag_2O and $AgCN$ is then treated with standard 0.2 N HNO_3 solution until the brown color disappears, and the amount used is recorded. The Ag_2O goes into solution according to the following reaction:

$$\underline{Ag_2O} + 2\ HNO_3 \rightarrow AgNO_3 + H_2O.$$

The cyanide, however, does not dissolve as it is only slightly soluble in dilute HNO_3 solution. The solution is then filtered to remove the cyanide, and titrated back with standard 0.1 N $NaOH$ solution to the point of the reappearance of a brown color. In this way the exact amount of acid required to react with the Ag_2O is found, and in consequence the amount of $NaOH$ originally present is calculable. Since this last end point is not distinct the reading is taken at the point of the first appearance of the brown color.

The precipitated $BaCO_3$ from the $Ba(NO_3)_2$ treatment is dissolved in standard HNO_3 solution and the amount used recorded. The solution is then boiled for five minutes and titrated back with standard $NaOH$ solution, using phenolphthalein as an indicator. The first reaction between the carbonate and acid is as follows:

$$\underline{BaCO_3} + 2\ HNO_3 \rightarrow Ba(NO_3)_2 + H_2CO_3.$$

This reaction is caused to go completely to the right by boiling the solution and decomposing the H_2CO_3 formed. Knowing the acid equivalent of the $NaOH$ solution the amount of HNO_3 required to react with the carbonate can be found. This then enables the calculation of the amount of carbonate originally present.

A sample taken from the charge after a run was analyzed according to the above system of analysis and gave the following results:

DATA AND CALCULATIONS

Sample taken - 15.5 grs.

1. Treated the sample with cold water- no hydrogen was evolved.

2. Added 75 c.c of 1 N $Ba(NO_3)_2$ solution, filtered and washed.

3. Made up the filtrate to 500 c.c and titrated 50 c.c of this solution with .05 N $AgNO_3$ solution.

Then $\frac{10 \times (2 \times .0463) \times 49 \times .05}{15.5} = 14.6\%$ NaCN

Added an excess of $AgNO_3$ solution.
Added 0.2113 N HNO_3 solution.
Amount used = 16.73 c.c.

Filtered and titrated back with NaOH solution, 1 c.c = 0.4982 c.c of HNO_3 solution.
Amount used = 19.60 c.c.

$$16.73 - (19.60 \times 0.4982) = 6.96 \text{ c.c of acid used.}$$

Then $\frac{10 \times 0.00696 \times 40 \times 0.2115}{15.5} = 3.62\%$ of NaOH.

4. Added HNO_3, 1 c.c = .0112 grams of Na_2CO_3, to the $Ba(NO_3)$ precipitate.

Amount used = 153.59 c.c.

Boiled and titrated excess with NaOH, 1 c.c = 0.4982 c.c of HNO_3 solution.

153.59 - (93.80 x .4982) = 106.86 c.c of acid used in reacting with the $BaCO_3$. This amount is equivalent to 106.86 c.c of 0.2115 N Na_2CO_3.

Then $\frac{53 \times 0.2115 \times 0.1069}{15.5} = 7.73\%$ NA_2CO_3

Analysis of the sample:- NaCN = 14.6%, NaOH = 3.62%, $NaCO_3$ = 7.73%.

A duplicate analysis of the above sample gave checks within 0.5 % for the NaOH, and within 0.3% for the carbonate and cyanide.

Entering gases

The gases passed into the reaction chamber consisted essentially of a mixture of carbon monoxide and nitrogen. The first experiments were carried out using practically pure (over 95%) carbon monoxide. This, of course, necessitated the consumption of a large amount of the gas before the equilibrium mixture of carbon monoxide and nitrogen was attained. In later experiments, basing the proportions on the analyses of the gases obtained in the equilibrium samples, it was found advisable to use a mixture of nearly equal amounts of carbon monoxide and nitrogen. Experiments in which nearly pure carbon monoxide was admitted to the bomb, and others using a mixture of equal amounts of carbon monoxide and nitrogen would then enable the equilibrium of the reaction to be approached both from the nitrogen and the carbon monoxide side; for it was found that the nitrogen in the equilibrium gas mixture at about 1000°C was considerably less than 50%.

The general arrangement of the apparatus for a typical run is shown in Fig. V. In this figure, A is a container for the entering gaseous mixture, and is equipped with a manometer. The two-way stop cock B enabled the use of any other gas without disconnecting the container. Two of the towers shown at C contain alkaline pyrogallol, and the other two concentrated sulphuric acid; these free the entering gas from carbon dioxide, oxygen and moisture. The stop cock D enables the rinsing of the washing towers with the gas before starting a run. The pressure in the reaction chamber within the furnace E is measured by the mercury manometer G, and desired vacuum being attained by means of a pump connected at F. H and I are the sample tubes and gas analysis apparatus respectively.

A typical run consists of the following operations:

1. Mixing the charge to be used in the bomb and filling the

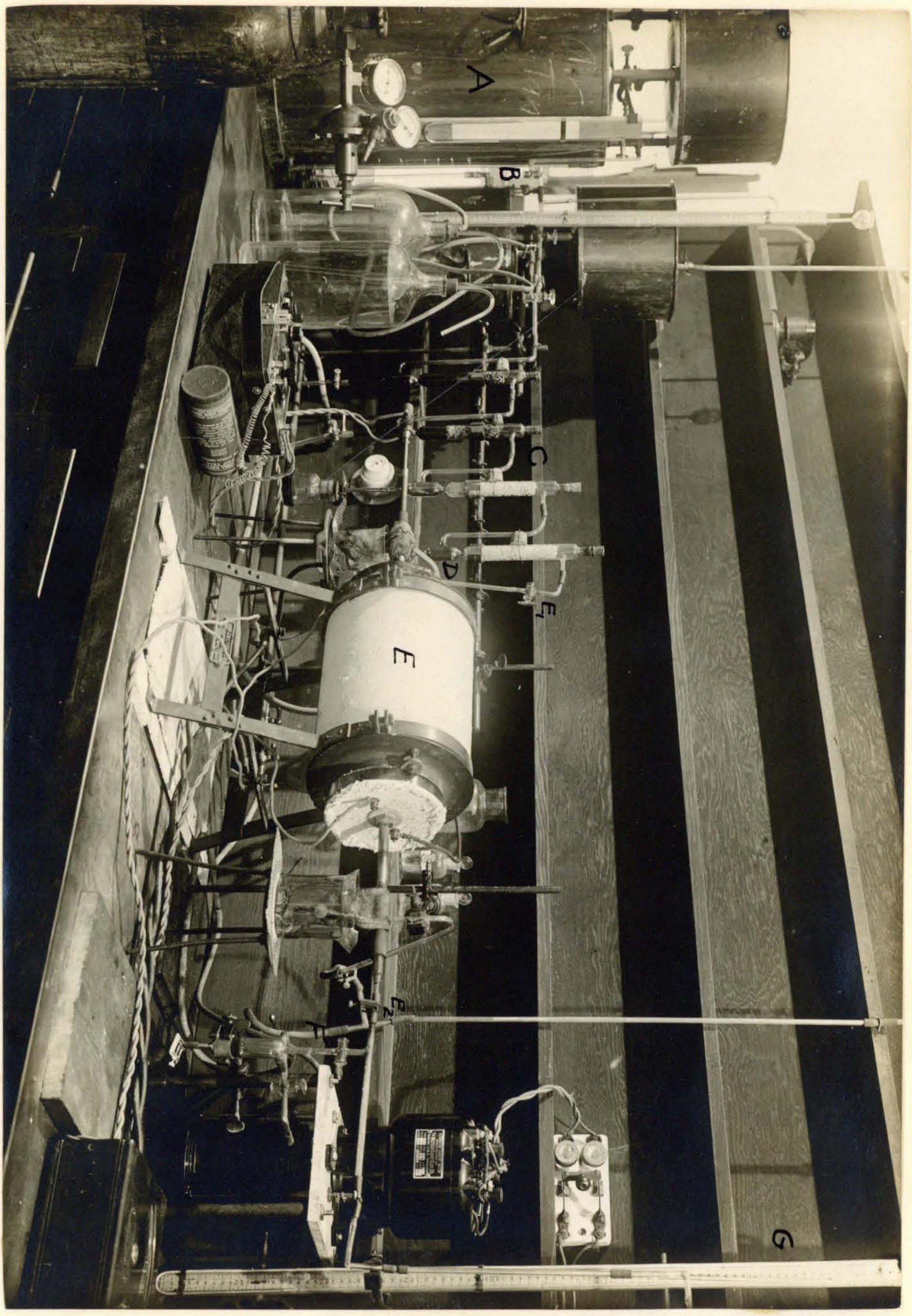

Figure V.a.

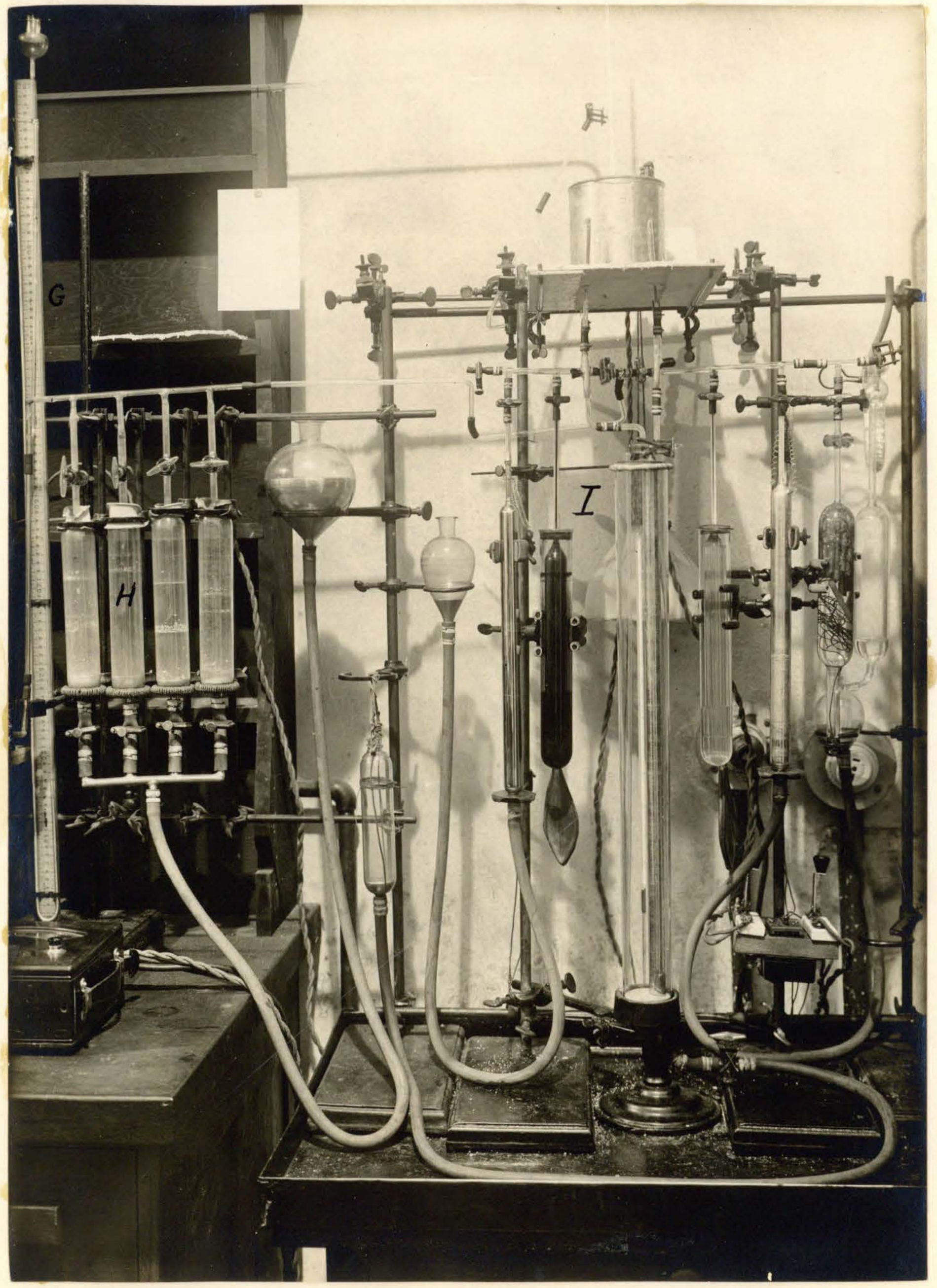

Figure V.b.

gas reservoir with the proper gas mixture.

2. Filling and welding the reaction chamber with subsequent tests for leaks throughout.

3. Pumping out of the bomb the gases which are formed during the five or six hour heating period, in which time the temperature rises from room temperature to about 1000°C. The proportions of nitrogen and carbon monoxide in this gas depend on the proportions of cyanide and carbonate present in the original charge.

4. Admitting the gas mixture to the bomb until equilibrium at the desired temperature is attained.

5. Drawing the samples from the equilibrium mixture. Two general methods were employed. First, the flow method, which required from twenty to forty- five minutes, in which the gases are admitted very slowly at slightly over atmospheric pressure and drawn from the bomb at practically the same pressure, thus insuring the formation of an equilibrium mixture. This method was finally abandoned as the concentrations of the CO and N_2 gases were thought to change as they gradually passed from a white heat to the cooler end of the bomb. To obviate this difficulty a second method was devised. The charge was allowed to come to equilibrium with the gases present in the bomb. The bomb was then cut off from the entering gas by closing the stop cock E_1 and the gases within the bomb were allowed to escape into the previously evacuated sample tubes H by quickly opening the stop cock E_2. This stop cock was then closed, and E_1 opened slowly, preparatory to taking another sample.

The equilibrium gas mixture samples were obtained in about 2 to 3 seconds in this manner and probably more nearly represented the true equilibrium mixture.

6. The analysis of the equilibrium gas samples, as soon as possible after taking, to enable a better control of the run and to lessen the possibility of contamination by leakage. The average time consumed in making an analysis with the cupric oxide tube apparatus was about three quarters of an hour. It was impossible to make runs longer than 40 to 48 hours; at the end of this time the iron bomb usually oxidized through and developed leaks.

The results relating to the determination of the equilibrium constant are tabulated in Table II. Each run is separately shown and the type of analysis apparatus indicated. Examination of the table reveals the fact that the discrepancies in the gas analyses are large, and that in many cases accuracy sufficient for a useful determination of the value of K was not obtained.

Experiment IV gave probably the best results of the series, and upon the data obtained in this experiment the calculation of the equilibrium constant and other data is based, not with the idea of establishing accurate values, but more to obtain a general knowledge of the prevailing conditions.

Calculations

The derivation of the heat of reaction is as follows:

From the data recorded in Exp. IV, the table given below is obtained:

T°C	K	$\log_{10}$ K
973	9.47×10^3	3.9763
989	19.7 "	4.2945
1008	32.5 "	4.5119
1010	41.3 "	4.6160
1010	31.9 "	4.5038
1012	45.0 "	4.6532
1016	64.8 "	4.8116
1016	29.5	4.4698

Experiment	I				II					III				
Charge mixture	NaCN 4 grs. C 4 " Na_2CO_3 16 " Fe 16 "				NaCN 30 grs C 20 " Na_2CO_3 16 " Fe 16 "					NaCN 30 grs C 20 " Na_2CO_3 16 " Fe 16 "				
Sample	A_1	B	B	C	A	B	C	D	E	O	A	B	C	D
Pressure	745	757	756	754	747	747	747	746	729	748	748	748	748	748
Time of taking	45 min.	30 min	30 min.	30 min	35 min.	42 min	55 min	63 min	— —	inter-val	15 min.	7 min	12 min	21 min
°C Temperature	920	898	898	898	—	—	—	—	—	— to 980	980	980	980	980
Type of analysis apparatus	combustion with O_2	"	"	"	"	"	"	"	"	"	"	"	"	"
% CO_2	1.5	8.6	14.8	13.1	0.0	0.0	0.0	0.7	1.4	1.0	4.1	5.5	4.8	5.3
% CO	0.7	35.5	43.4	59.5	4.1	2.3	2.7	10.7	3.7	15.7	62.4	74.5	79.2	78.1
% N_2	76.3	49.4	40.0	29.5	71.7	70.6	83.8	70.3	86.4	72.4	22.7	12.5	10.0	11.4
% O_2	21.2	0.1	0.1	0.9	0.8	0.4	0.2	0.1	2.0	0.0	3.1	0.6	0.9	0.3
% H_2	—	5.0	1.8	1.3	23.0	29.8	22.0	19.5	6.9	10.9	7.3	6.8	5.2	4.9
Total	99.7	98.6	100.3	99.3	99.6	103.1	108.7	101.3	100.4	100.0	99.6	99.9	100.1	100.0
CO/N_2														
$(CO)^3/N_2$	4.49×10^{-3}	9.06×10^{2}	2.04×10^{3}	5.49×10^{3}	9.61×10^{-1}	1.71×10^{-1}	2.35×10^{-1}	1.77×10	5.86×10^{-1}	5.35×10	1.07×10^{4}	3.30×10^{4}	4.93×10^{4}	4.17×10^{4}
Entering gas.					>90% CO, <10% N_2					>90% CO, <10% N_2				

Experiment	IV						V									
Charge mixture	NaCN 183.3 grs C 85.0 " Na_2CO_3 275.0 " Fe 430.8 "						NaCN 183.3 grs C 85.0 " Na_2CO_3 275.0 " Fe 430.8 " Used 350 grs. of the mixture!									
Sample	A	B	C	D	E	F	A	B	C	D	E	F	G	H	I	J
Pressure	741	738	741	750 to 216	751 — —	750 — —	783	783	784	783	783	783	784	784	784	784
Time of taking	25 min	25 min	27 min.	10 sec	10 sec	10 sec	29 min	20 sec	5 sec	3 sec	2 sec	2 sec	2 sec	2 sec	2 sec	2 sec.
°C Temperature	1050	1050	1049	1040	1004	985	1012	1012	1010	1010	1012	1008	973	989	1016	1016
Type of analysis apparatus	CuO tube	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
% CO_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
% CO	77.6	83.3	80.5	84.2	85.4	80.9	58.7	66.1	83.7	79.7	84.1	81.2	66.1	75.8	88.3	79.0
% N_2	16.0	14.0	16.2	14.3	10.6	15.9	38.7	31.5	14.2	15.9	13.2	16.5	30.5	22.1	10.6	16.7
% O_2	0.7	0.2	0.0	0.0	0.0	0.0	0.0	1.4	0.0	1.5	0.2	0.2	1.1	0.2	0.0	2.7
% H_2	6.0	2.5	3.4	1.7	4.0	3.5	2.8	1.7	2.1	2.9	2.4	2.1	2.2	1.8	1.2	1.6
Total	100.3	100.0	100.1	100.2	100.0	100.3	100.2	100.7	100.0	100.0	100.0	100.0	99.9	99.9	100.1	100.0
CO/N_2	4.85	5.95	4.93	5.9	8.06	5.09	1.52	2.10	5.90	5.01	6.37	4.92	2.17	3.53	8.33	4.73
$(CO)^3/N_2$	2.92×10^{4}	4.13×10^{4}	3.22×10^{4}	4.18×10^{4}	5.87×10^{4}	3.33×10^{4}	$.522 \times 10^{4}$	$.918 \times 10^{4}$	4.13×10^{4}	3.19×10^{4}	4.50×10^{4}	3.25×10^{4}	$.947 \times 10^{4}$	1.97×10^{4}	6.48×10^{4}	2.95×10^{4}
Entering gas.	>90% CO, <10% N_2						CO 49% N_2 46.2% CO_2+O_2 3.8% H_2 1.0%									

Experiment	VI											
Charge mixture	NaCN 180 grs C 100 " Na_2CO_3 120 " Fe 400 " Charge used in form of pencils. End plugs used in Exp's. IV, V, VI											
Sample	A	B	C	D	E_1	E_2	F_1	F_2	G_1	G_2	H_1	H_2
Pressure	744	744	744	744	same 744	744	same 744	744	same 748	748	same. 748	748
Time of taking	10 sec	4 sec	2 sec	2 sec	2 sec	2 sec	5 sec	5 sec	2 sec	2 sec	4 sec	4 sec.
°C Temperature	1000	1005	1014	1014	1010	1010	1012	1012	1013	1013	1022	1022
Type of analysis apparatus	CuO tube Pyrogallol KOH.	"	"	"	"	"	"	"	"	CuO tube Phos. KOH	CuO tube $CuCl_2$ Pyrogallol	CuO tube Phos. KOH.
% CO_2		Oxygen and CO_2 removed together as CO_2+O_2										
% CO	0.0	5.6	0.3	3.4	3.0	0.8	2.9	1.5	0.1	0.5	0.8	0.4
% N_2	48.8	51.1	53.4	56.0	62.7	65.3	68.5	58.0	39.1	35.4	50.0	44.6
% O_2	47.8	32.8	31.0	29.9	30.1	28.9	27.5	53.3	55.9	56.8	49.2	46.3
% H_2	3.7	10.6	15.3	10.3	6.8	5.0	2.9	7.3	4.5	7.3	—	7.5
Total	100.3	100.0	100.0	99.6	99.9	100.0	100.0	100.1	100.0	100.0	100.0	100.0
CO/N_2	1.02	1.56	1.72	1.87	2.08	2.26	2.49	1.74	.70	.62	1.02	.75
$(CO)^3/N_2$	2.43×10^{3}	4.04×10^{3}	4.91×10^{3}	5.88×10^{3}	8.18×10^{3}	9.62×10^{3}	7.47×10^{3}	5.86×10^{3}	1.07×10^{3}	$.784 \times 10^{3}$	2.54×10^{3}	1.92×10^{3}
Entering gas.	CO 53.7% N_2 44.3% CO_2+O_2 0.9% H_2 1.1%											

TABLE II

The values of T and $\log_{10}K$ are plotted in Fig. VI. They may be assumed with an accuracy equal to that of the data, to lie on the straight line shown. Assuming this linear relation, the slope of the curve will be found from the plot to be 0.0176. Substituting this value for $\frac{d \log_{10}K}{dT}$ in the equation

$$\frac{d \log_e K}{dT} = 2.303 \frac{d \log_{10}K}{dT} = \frac{\Delta H}{RT^2}$$

gives $\Delta H = 0.0176 \times 2.303 \times 1.98 \times (1273)^2 = 130{,}000$ calories

for the heat change of the reaction

$$Na_2CO_3 + N_2 + 4C \rightleftarrows 2\,NaCN + 3\,CO \text{ at } 1000° C.$$

From Landolt-Börnstein-Roth Tabellen, pgs. 859 and 855, the heats of formation of NaCN, CO, and Na_2CO_3 from their elements are given as 22,600, 29,000 and 270,800 respectively. From these data the heat change of the Bucher reaction at room temperature can be calculated as

$$H = 270{,}800 - 2(22600) - 3(29{,}000) = 138{,}600 \text{ cal.},$$

a value in fair agreement with that given above. The agreement becomes still better if account is taken, in the following manner, of the fact that one value refers to room temperature and the other to 1000°C.

The molal heat capacity of Na_2CO_3 is given by Landolt Börnstein, pg. 758, as $0.27 \times 106 = 29$ cal. per degree. The molal heat capacity of NaCN is not given but may be calculated by the formula given by Noyes (7) to be $M\bar{C}_{P_{NaCN}} = 6.2 + 1.8 + 6.2 = 14.2$ cal.

The molal heat capacities of carbon, nitrogen and carbon monoxide at high temperatures are given in Landolt-Börnstein, pgs. 751 and 773 as 4.3, 3.6 and 6.8 respectively. The change in molal heat capacity when the reaction $Na_2CO_3 + N_2 + 4\,C \rightleftarrows 2\,NaCN + 3\,CO$ occurs will therefore be $29. + 2(3.6)$ $4(4.3) - 2(14.2) - 3(6.8) = 4.2$ cal. The heat content decrease attending the

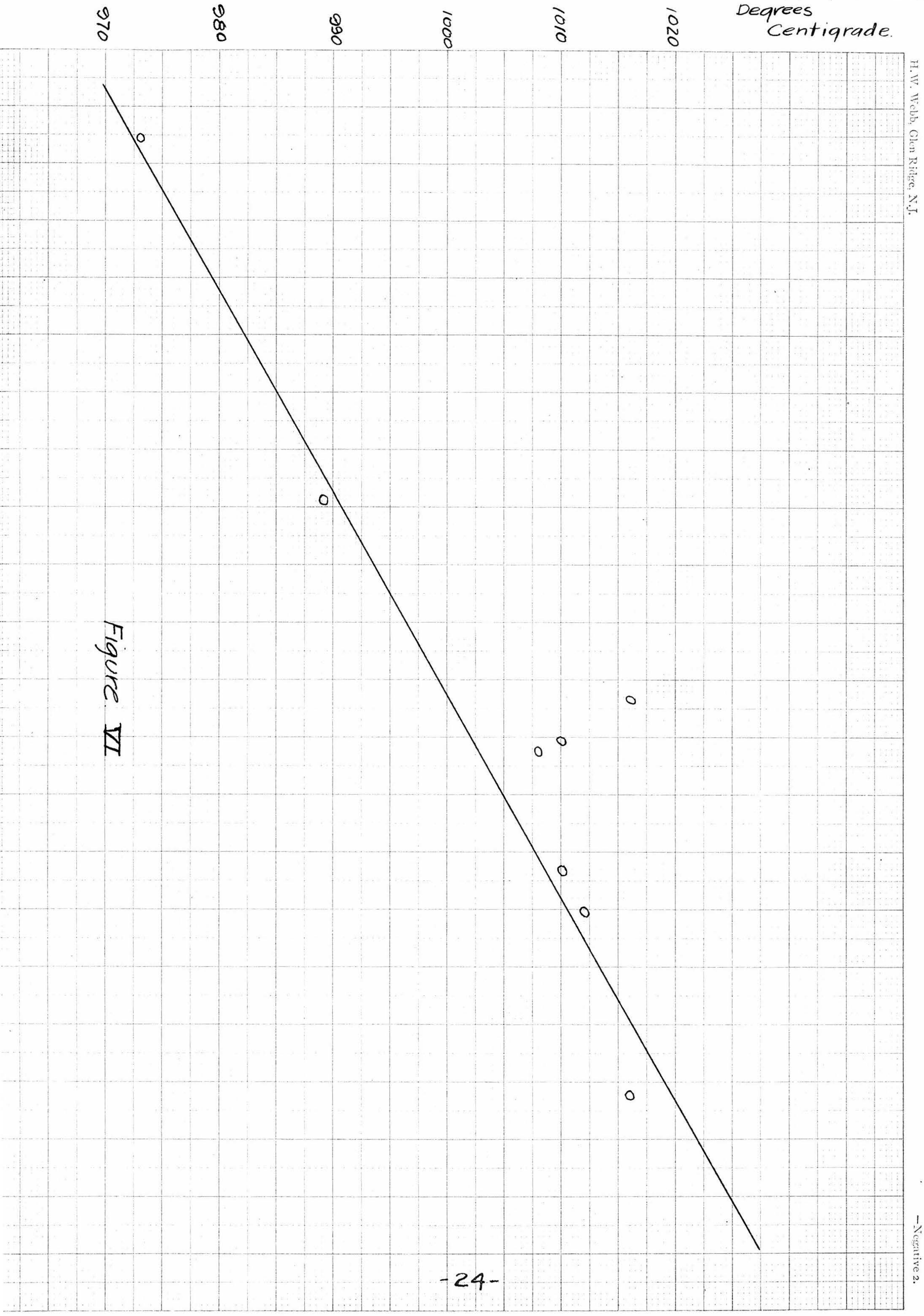
Degrees Centigrade.
970
980
990
1000
1010
1020
H.W. Webb, Glen Ridge, N.J.
—Negative 2.

Figure VI

the reaction at 1000°C will therefore be approximately 4.2 x 1000 = 4200 calories less at 1000°C than at room temperature, if no account is taken of the latent heat of fusion of sodium carbonate and sodium cyanide. The value, -138,600 cal. from Landolt-Börnstein should on these assumptions be decreased by 4,200 cal., giving - 134,400 cal. as the heat content decrease at 1000°C. This figure compares favorably with that (-130,000 cal.) derived from the experimental data of this thesis. The mean value, -132,000 cal., may be assumed provisionally for the heat content decrease near 1000°C. Using this value the ratio of the equilibrium constant K_T at any absolute temperature T, to the constant K_{1273} at 1273°A, may be calculated, by use of the equation

$$\log \frac{K_{T_1}}{K_{T_2}} = \frac{\Delta H}{2.303R} \frac{T_1 - T_2}{T_2 T_1}$$

Taking K_{1000} as 2.9×10^4 (see plot Fig.VII) gives

$$\log_{10} K_T = \frac{132,000}{(2.3)\,(1.98)} \frac{T-1273}{1273.T} + \log K_{1273} = 22.8\left(1-\frac{1273}{T}\right)+4.45$$

The use of this formula, assuming the heat of reaction to remain constant over the temperature range, gives the following values for K at various temperatures:

T °C	K
800	1.62
850	24.6
900	321.
950	3290.
1000	29,000.
1050	206,000
1100	1,294,000

SUMMARY

In this thesis has been presented a description of the apparatus and methods employed in a determination of the equilibrium conditions of the Bucher reaction, $Na_2CO_3 + N_2 + 4C \longrightarrow 2\ NaCN + 3O$, and their dependence upon the temperature.

The results obtained, while not entirely satisfactory, show that the equilibrium constant K of the reaction is about 1.6 at 800°C, 320 at 900°C; 3×10^4 at 1000°C, and 1.2×10^6 at 1100°C; and that the heat content decrease when the reaction goes toward the production of sodium cyanide is 132,000 ± 2000 calories.

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