

THE REACTION BETWEEN  
NITROGEN AND METHANE  
IN THE SILENT ELECTRIC DISCHARGE

Thesis

by

Lester O. Warner

In partial fulfillment of the requirements  
for the degree of Bachelor of Science  
in Chemical Engineering.

CALIFORNIA INSTITUTE OF TECHNOLOGY

Pasadena, California.

1922

THE REACTION BETWEEN NITROGEN AND METHANE  
IN THE SILENT ELECTRIC DISCHARGE

Introduction

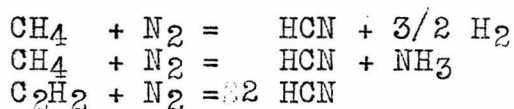
The importance of nitrogen compounds has been recognized for more than twenty years, yet it has only been during the last five years that any serious attempts have been made in this country to develop the existing nitrogen fixation processes upon a commercial scale. This has been due to a diffidence towards the industry by financial leaders and a serious deficiency of technical data which is essential to the commercialization.

At the present time the cyanamide and Haber processes are the most promising. Ammonia is the principal product from both of these. The commercial production of cyanides is almost solely dependent upon the fusion of calcium cyanamide with carbon and sodium chloride. Another method which has been tried upon a commercial scale with some success is the Bucher process<sup>1)</sup> by which sodium cyanide is leached from an electric furnace product. The power requirements are

1) J.E.Bucher, J.Ind.Eng.Chem., 9, 233-253 (1917)  
A.H.White, J.Ind.Eng.Chem., 11, 231-237 (1917)

about the same as for the Haber process, and the operating temperature is nearly 1000°C. The charge contains considerable sodium carbonate which causes rapid corrosion of the furnace. The demand for liquid hydrocyanic acid has greatly increased during the last few years due to its use as a fumigant and in rodent control. This demand is supplied at present by treating crude cyanides with strong sulfuric acid and redistilling the product.

The Lipinski hydrocyanic acid process<sup>1)</sup> has been given no attention commercially, although a great deal of experimental work has been done. A mixture of pure nitrogen and some hydrocarbon gas such as methane, ethane, ethylene or acetylene, diluted with hydrogen, is subjected to a high tension spark discharge which causes a reaction of the following type to occur.



Lipinski<sup>2)</sup> in 1911 reported that mixtures of CH<sub>4</sub>, N<sub>2</sub> and H<sub>2</sub> were quantitatively converted into HCN when passed over a 2000 volt arc between platinum electrodes. Carbon was deposited from mixtures containing

- 1) R.C. Smith, Unpublished thesis, California Institute of Technology, (1920)
- 2) A.V. Lipinski, Zeitsch. Electrochem. 17, 761-764 (1911)

over 20 percent methane. This was later claimed to be the original work of Moscicki<sup>1)</sup>. Briner and Baerfuss<sup>2)</sup> in 1920 obtained a concentration of 0.75% HCN by volume in a mixture of one part CH<sub>4</sub> and five parts N<sub>2</sub>. The best results were obtained with a potential of 505 volts between platinum electrodes and with the gas at a pressure of 100 mm. of mercury. The yield was 7.39 grams of HCN and 0.48 grams of NH<sub>3</sub> per kilowatt-hour.

The greatest difficulties with this process seem to be the deposition of carbon from undiluted mixtures, probably due to thermal decomposition of the hydrocarbon in the spark. The electrical efficiency would naturally be low and such a process is of little value in this country. Dr. A.A. Noyes suggested that if the silent discharge would effect the desired reaction, the yields could be materially increased as the electrical energy consumption is quite low for large gas capacity.

#### Purpose

It is the purpose of this work to investigate the Lipinski reaction in the silent discharge, and if

1) I. Moscicki, Zeitsch. Electrochem. 17, 877 (1911)

2) E. Briner and A. Baerfuss, Helvetica Chim.

Acta., 2, 663-666 (1919)

Synopsis, Chem. and Met. Eng. 22 329 (1920)

the same reaction occurs, to study the conditions which will give the greatest efficiency.

### Historical

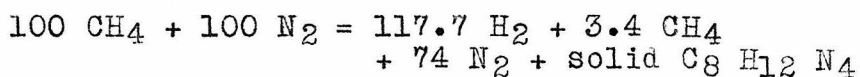
The earliest record of the effect of the silent discharge upon  $N_2$  and  $H_2$  was reported by Thénard<sup>1)</sup> in 1873 who stated that the reaction was induced by the discharge. At the same time he found that  $C_2H_4$  polymerizes in the silent discharge. Berthelot<sup>2)</sup>, three years later, reported that  $H_2$  and  $N_2$  react and that  $NH_3$  is decomposed in the dark discharge to produce an equilibrium mixture containing 3%  $NH_3$ . Methane, ethane and ethene yield a little acetylene, free  $H_2$  and resinous condensation products, as well as the liquid condensation product discovered by Thénard, (loc. cit.)

Löb, in his book, "Electrochemistry of Organic Compounds", reviews some experiments of Berthelot<sup>3)</sup> in which he subjected a mixture of equal parts of  $N_2$  and  $CH_4$  to a closed ozonizer discharge for 24 hours.

The following equation is typical for all hydrocarbons:

- 1) Thénard, Compt. rend., 76, 1508 (1873)  
Review by J.N. Collie, Journ. Chem. Soc. 1905, T 1540-48
- 2) Berthelot, Bull. Soc. Chim. 26, (2) 101-104  
Abstract, Journ. Chem. Soc. 1876, A(2), 596
- 3) Berthelot, Compt. rend., 126, 567 (1898)

used. No evidence of HCN or NH<sub>3</sub> was reported.



Gaudechon<sup>1)</sup> found that cyanogen is decomposed in the silent discharge with the liberation of N<sub>2</sub> and a brown solid substance is formed whose composition varies with the pressure, capacity of apparatus and potential. It is not a simple polymerization product of cyanogen.

Le Blanc and Davies<sup>2)</sup> found the rate of decomposition of dry NH<sub>3</sub> in the silent discharge at constant temperature and current to be nearly proportional to the pressure. The temperature coefficient is small, the rate being doubled by a temperature rise of 100°C. The rate is not directly proportional to the current as expected, but is nearly doubled by an increase of one-third in the current. Dilution with H<sub>2</sub> decreases the rate of decomposition, but N<sub>2</sub> increases it. The luminosity of the discharge is increased by N<sub>2</sub>, but not by H<sub>2</sub>. The law of mass action was found not to hold.

- 1) Gaudechon, Compt, rend., 143, 117-119 (1906)  
Abstract, Journ. Chem. Soc., 1908, A (1), 731
- 2) Max LeBlanc and John. Davies, Zeitsch.  
Electrochem. 14, 361-366 (1908)  
Abstract, Journ. Chem. Soc., 1908, A (2), 653

Briner and Durand<sup>1)</sup> investigated the effect of both the spark and the silent discharge upon a mixture of  $N_2$  and  $C_2H_6$  at a temperature of  $-78^\circ C$ . The silent discharge gave less HCN and more condensed hydrocarbons than the spark discharge. The spark discharge produced carbon,  $H_2$ , HCN,  $NH_3$  and higher hydrocarbons. In some experiments with  $N_2$  and  $C_2H_2$ , HCN was found to predominate over  $NH_3$ . The silent discharge produced no carbon from pure  $C_2H_6$  at  $-78^\circ C$ .

#### Theoretical

The nature of the various electric discharges has not been well explained and much confusion has resulted from the inexact use of the terms, "electric discharge", "dark discharge", "brush discharge", "point discharge", etc., in reference to the silent discharge. The silent discharge is not silent, but consists of a multitude of minute sparks which cause a crackling.

E.K.Rideal<sup>2)</sup> in his book entitled, "Ozone", gives two volt-ampere curves taken from Toepler which are reproduced in figures 1 and 2.

1) Briner and Durand, Journ. Chim. Phys. 7, 1-30  
Abstract, Journ. Chem. Soc. 1909, A (1), 125

2) E.K.Rideal, "Ozone", Constable and Co., London (1920)

Although these curves are for point to plate discharges, they will hold for the alternating current discharge.

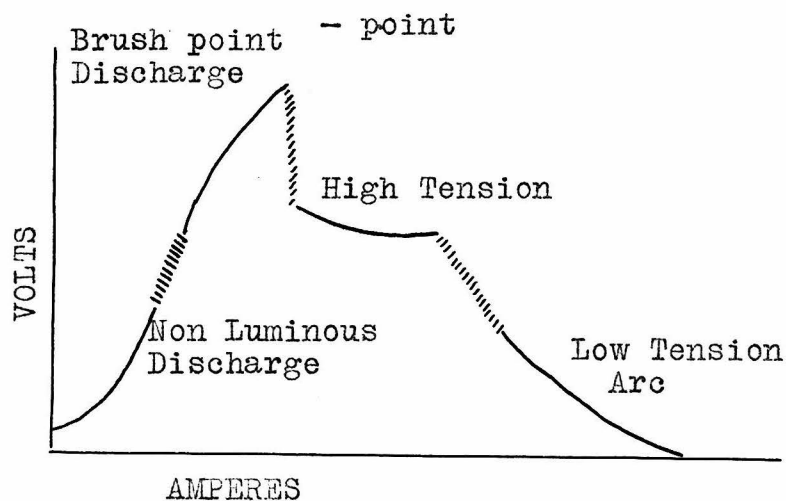


Fig. 1.

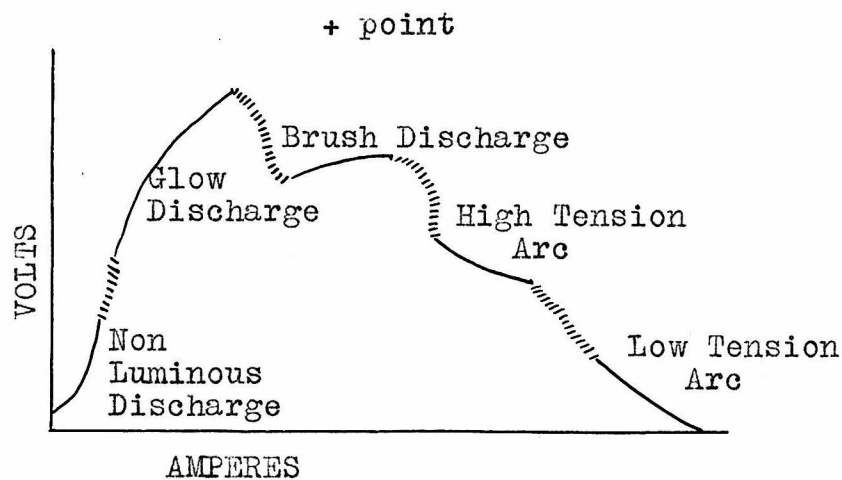


Fig. 2.



As the potential difference is gradually increased, an invisible dark discharge occurs at about one hundred volts. This dark discharge gradually changes to a visible glow, starting with a few bright spots in the discharge tube. No great increase in current occurs until the brush discharge starts. The corona discharge is shown as "glow discharge" in the figure, but the use of a large diameter inner electrode prevents the corona formation.

The base of the brush discharge produces the greatest amount of ozone. The insertion of a solid dielectric allows the electrodes to be brought closer together without forming an arc, thereby bringing the gas into the most active part of the discharge.

The mechanism by which the chemical reactions take place under the influence of the various electric discharges is not understood. This is true of ozone, but the conditions for formation have been fairly well established.

The ultra-violet radiation from the aluminum or iron spark appears to be a contributing factor, as the yield of ozone is greater when one of these metals is used as an electrode. However, most of the ozone formation is due to ionization resulting from the bombard-

ment of atoms by primary or secondary electrons.

That the electrons are largely of secondary origin, Lind<sup>1)</sup> shows from experiments of Warburg. One gram-equivalent of ozone, under favorable conditions, requires less than 100 coulombs instead of 96,500 which would be required if the ionization resulted solely from primary electrons. Reactions may take place when the ionized constituents are together under proper conditions, so that the equilibrium conditions would be dependent upon the ionization product. Anderegg<sup>2)</sup> has calculated the minimum potential necessary to ionize N on the basis of the quantum theory and he has obtained the value of 9 volts from recent data. Similarly, the minimum potential for ionization of O was set at 6.4 volts. Commercial operation of ozonizers is very satisfactory at 8000 volts, from which, by direct proportion, a potential of 11,300 volts should be sufficient for ionization of N in an ozonizer.

Another theory of the Lipinski reaction is based upon the existence of an active form of nitrogen.

- 1) S.C.Lind, "The Chemical Effects of Alpha Particles and Electrons", Chem. Cat. Co. (1921)
- 2) F.O.Anderegg, Science, 50, 49 (1919)  
Abstract, Chem. Abs., 13, 3090 (1919)

Strutt<sup>1)</sup> found that pure nitrogen, when subjected to the action of an electric discharge from a Leyden jar in an exhausted tube, underwent a change. The gas remained chemically active for a short period and reacted with acetylene to form cyanogen.

Wendt and Grubb<sup>2)</sup> recently announced that an active form of nitrogen had been obtained in a corona discharge of 20,000 volts from fine wires in pure nitrogen at atmospheric pressure. Under most favorable conditions as much as 4% is made active and reacts readily with  $H_2$  to form  $NH_3$  and with  $O_2$  to form nitrogen oxides. It is unlike Strutt's nitrogen which is obtained only at low pressures and which does not react with  $H_2$  or  $O_2$ . It forms slowly and persists for hours afterward. It has an odor resembling formaldehyde.

The concentration of ozone in the silent discharge is much greater than that corresponding to thermal equilibrium. A small increase in temperature, causes a very marked decrease in concentration, by increasing the rate of decomposition.

- 1) R.J.Strutt, Proc. Roy. Soc., 85A, 219-229 (1911)  
86A, 56-63, 262-269 (1911); 87A, 179-188 (1912)  
Abstract. Journ. Chem. Soc. 1911, A(2) 482 ;  
1912, A(2), 153; 447; 935
- 2) G.L.Wendt and A.C.Grubb, Report of St.Louis meeting of the Am. Chem.Soc., Chem. and Met. Eng.,  
22, 771 (1920)

The products of the Lipinski reaction,  $\text{NH}_3$  and  $\text{HCN}$ , are quite stable at ordinary temperatures, but the equilibrium concentrations are extremely small. An increase in temperature sufficient to produce a desirable concentration would cause a decided decomposition of methane. Refrigeration should be unnecessary as there are no high rates of decomposition involved.

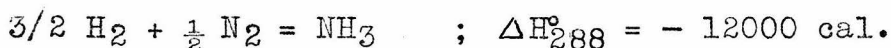
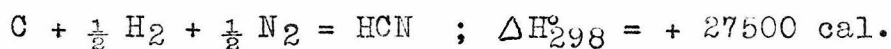
The fixation of nitrogen as  $\text{N}_2\text{O}_5$  in the silent discharge (corona) has been investigated by Harding and Mc Eachron<sup>1)</sup>. Air was passed through a discharge tube which differs from the usual ozonizer. The corona takes place between an aluminum tube six inches in diameter and an aluminum rod five eighths of an inch in diameter. To increase the corona and prevent the formation of a power arc, a glazed porcelain tube one half inch thick was placed between the two electrodes. The potential used was approximately 30 kilovolts. The results obtained show the greatest yield at a critical velocity of about six liters per minute under a pressure of 780 mm. of mercury, the highest pressure used. Under these conditions the yield was 9.8 grams  $\text{HNO}_3$  per kilowatt-hour.

1) C. Francis Harding and K. B. Mc Eachron, Journ. Am. Inst. Elec. Eng. 39, 405-415 (1920)

The silent discharge does not appear to activate  $N_2$  and cause it to react in the same manner that the high tension spark does. It is possible that HCN may have been an intermediate product in the formation of  $C_8H_{12}N_4$  reported by Berthelot, but neither of the Lipinski reaction products were reported.

Ammonia appears to be produced to the extent of about 3% by volume in pure nitrogen and hydrogen, but this may be due, not to nitrogen activation, but to an active form of hydrogen<sup>1)</sup>. Active hydrogen is present in the glass tube ozonizer at 10 to 20 kilovolts potential to the extent of only 0.01%, but its reaction with nitrogen has been demonstrated.

In order to calculate the equilibrium concentrations and the energy requirements of the Lipinski reaction, use was made of data from "Landolt-Börnstein".

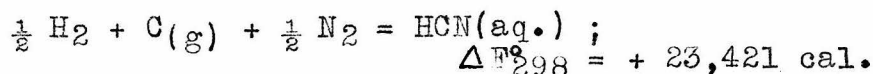


Lewis and Brighton<sup>2)</sup> have calculated the free

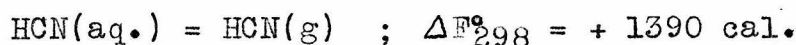
1) G.L.Wendt and R.S.Landauer, Journ. Amer. Chem. Soc., 42, 930-945 (1920); 44, 510-520 (1922)

2) G.N.Lewis and T.B.Brighton, Journ. Amer. Chem. Soc., 40, p. 489 (1918)

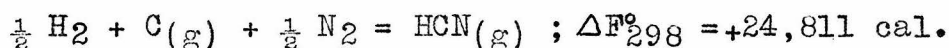
energy of the following reaction:



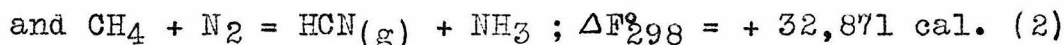
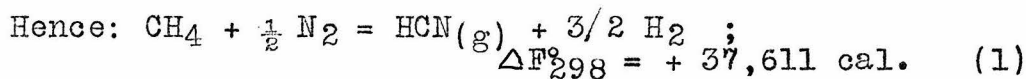
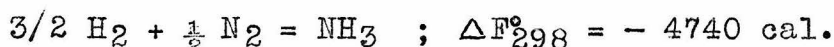
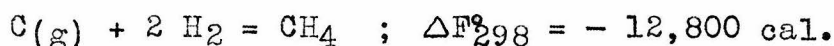
The approximate free energy of the following reaction was obtained by Lewis and Keyes<sup>1)</sup>.



By addition, the desired equation is obtained.



The free energy of methane is given by Lewis and Randall<sup>2)</sup>, and that of ammonia by Lewis and Adams<sup>3)</sup>.



The equilibrium constant is readily obtained from the relation  $\Delta F = - RT \ln K$ .

$$\frac{(p_{\text{H}_2})^{3/2} (p_{\text{HCN}})}{(p_{\text{CH}_4}) (p_{\text{N}_2})^{1/2}} = K = 7.36 \times 10^{-28} \quad (3)$$

- 1) G.N.Lewis and D.B.Keyes, Journ. Amer. Chem. Soc., 40, p.475 (1918)
- 2) G.N.Lewis and Merle Randall, Journ. Amer. Chem. Soc., 37, p.469 (1915)
- 3) G.N.Lewis and E.Q.Adams, Journ. Amer. Chem. Soc., 37, p.2309 (1915)

$$\text{and } \frac{(P_{\text{NH}_3}) (P_{\text{HCN}})}{(P_{\text{CH}_4}) (P_{\text{N}_2})} = K = 9.68 \times 10^{-25} \quad (4)$$

On the basis of equation (4) the thermal equilibrium concentration of  $\text{NH}_3$  or  $\text{HCN}$  would have a maximum value of  $4.9 \times 10^{-11} \%$  for  $25^\circ\text{C}$ .

### Experimental

The nitrogen was prepared by passing air and  $\text{H}_2$  over red hot  $\text{Cu}$  and  $\text{CuO}$ <sup>1)</sup>. Natural gas containing 85% methane was also passed through the tube of  $\text{Cu}$  and  $\text{CuO}$  to remove small amounts of oxygen, due to air, from the gas. The mixture was later found to contain 60%  $\text{N}_2$ . A temperature of  $600^\circ\text{C}$ ., measured by an iron-constantan thermocouple was most satisfactory for the combustion of  $\text{O}_2$  in air. A temperature of  $475^\circ\text{C}$ . caused no appreciable decomposition of  $\text{CH}_4$  and the small amount of  $\text{O}_2$  in the natural gas was quickly removed. The gas was stored in a large carboy over "transil" oil, from which it was displaced by air-free water with a constant pressure syphon. The gas was dried over  $\text{CaCl}_2$  before passing through the discharge tube.

A number of discharge tubes were constructed and tested as ozonizers before one was found satisfactory.

1) Geo. A. Hulett, Journ. Amer. Chem. Soc.,  
27, 1415-1418 (1905)

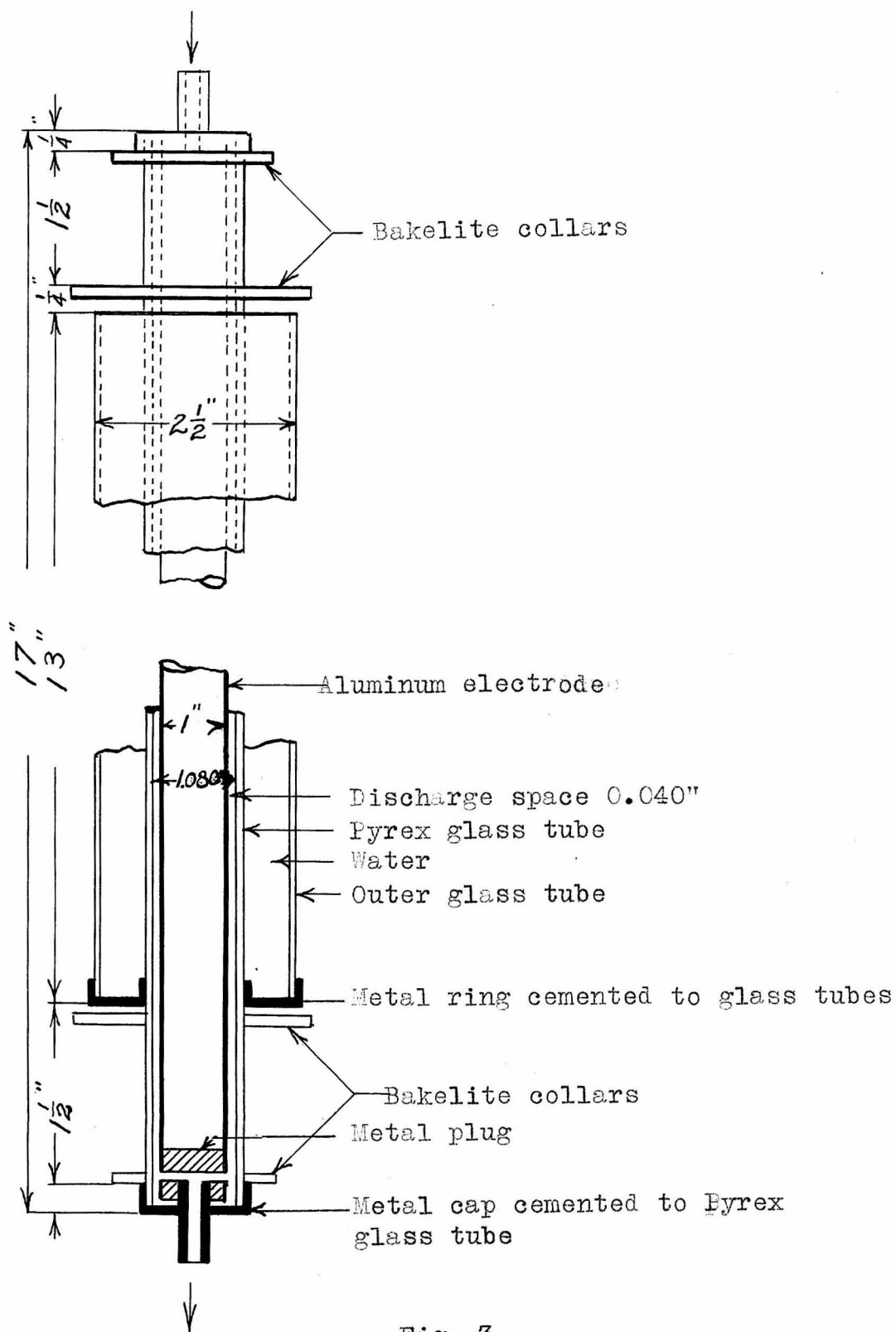


Fig. 3.



The tube used is shown in detail in fig. 3. Pyrex glass tubing was used as the dielectric as it withstands a greater potential difference and is also to be obtained with a more uniform cross section than soft glass tubing. Care was taken to keep the gas space in the tube small, permitting a rapid removal of products from the discharge with slow rates of flow. The inner electrode was made of one inch aluminum tubing supported by metal plugs. The distance between the electrodes through which the discharge took place was 1.0 mm. (0.040 in.). Water was used to cool the dielectric and was also used for the other electrode.

As there was no high voltage transformer available, one was constructed as a part of this work. A tertiary coil having an exact ratio to the secondary was provided so that a voltmeter could be used to obtain the approximate voltage. The primary was tapped to provide for secondary voltage control without the use of resistance. The maximum voltage obtainable was 16,000 volts.

The  $\text{NH}_3$  was absorbed directly in Nessler's reagent in several preliminary runs, making a test for HCN impossible. A large yellow precipitate formed which did not resemble that formed by  $\text{NH}_3$ . It may

have been the white precipitate (colored by the ammonia) which acetylene forms in Nessler's reagent. It was avoided entirely by absorbing the  $\text{NH}_3$  in dilute  $\text{HNO}_3$  and removing the other gas by heating and drawing a slow current of air through the scrubbers. The acid solution was then neutralized with  $\text{NaOH}$  and 1 cc. of Nessler's reagent added. A blank was made to which an ammonium chloride solution was added until the small precipitates were matched. The solution contained approximately 0.1 mg. of  $\text{NH}_3$  per cc. A dilute standardized solution of  $\text{NH}_4\text{OH}$  was used in the blank for run 9 and the result obtained was more accurate than in the previous tests.

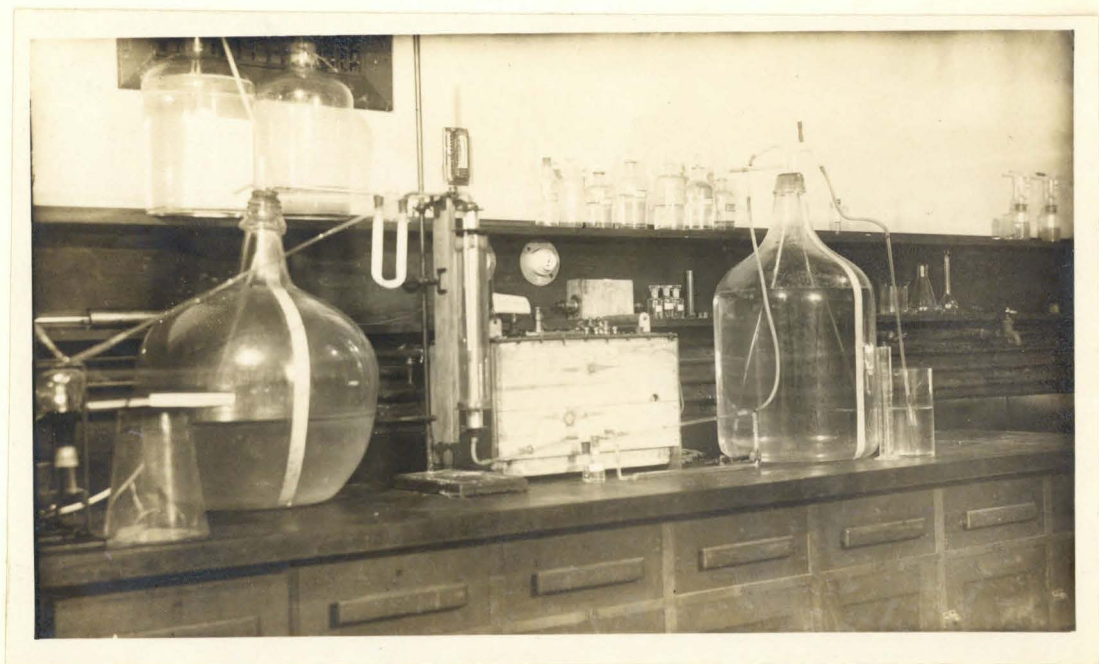
The  $\text{HCN}$ , after passing through the acid, was absorbed by dilute  $\text{NaOH}$  in a horizontal tube scrubber. One drop of standardized  $1/20 \text{ N}$   $\text{AgNO}_3$  gave a permanent precipitate of  $\text{AgI}$  in the acidified solution to which  $\text{KI}$  had been added. For this reason, no  $\text{HCN}$  was reported in most of the runs, although small amounts may have been present. The Liebig method of determining  $\text{HCN}$  was not extremely sensitive, so the phthalin reaction<sup>1)</sup> was used in run 9. The test was sensitive to less than 0.001 mg. of  $\text{HCN}$  if the solution is first

1) C.F. Ritchie, Thesis, California Institute of Technology. (1922)

made acid and then alkaline, but it is not sensitive otherwise. The following table gives the results of several runs.

Run No.	Potential Volts	Rate cc./hr.	Gas Vol. cc.	% by Vol. NH <sub>3</sub>	Vol. HCN	Av. Temp. °C.
4	14,600	260	130	0.08	—	26.5
5	14,600	530	265	0.06	—	23.0
6	5,050	163	163	0.04	—	22.3
7	5,050	1062	354	0.03	—	23.8
8	16,000	83	83	0.14	—	30.9
9	16,000	95	95	0.089	0.003	31.5

A yellow aromatic substance was deposited on the aluminum electrode and on the inside of the Pyrex tube. It was tacky and quite soluble in cold water. A similar substance was condensed from illuminating gas (oil gas) when passed through the discharge.



Photograph of Apparatus Used.

### Conclusions

The concentration of  $\text{NH}_3$  was greatest under the highest potential used and the rate of formation was extremely low, requiring slow rates of flow. Lack of time did not permit a study of the effect of temperature. The extremely small amounts of  $\text{NH}_3$  and  $\text{HCN}$  found indicate that radical changes in the experimental conditions are needed to secure results comparable to those obtained by other electrical methods. The silent electric discharge is not satisfactory for the Lipinski reaction and in future investigations, attention should be directed toward higher voltages and the effect of the corona discharge from fine wires. The high tension spark, if spread by an electromagnetic or electrostatic field, would present a greater surface to the gases, or pressures greater than atmospheric would increase the amount of gas in contact with the arc.

I wish to express my appreciation for the suggestions and help rendered by Dr. W.N.Lacey, under whose direction the work was done. Also for the suggestions of various members of the department and for the assistance of Mr. Barnewolt of the Standard Oil Co. who secured the natural gas used.