

SOME EXPERIMENTS ON THE
SYNTHESIS OF AMMONIA FROM NITROGEN AND HYDROGEN

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BY

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CONSIDERATION OF THE N, H, NH₃ EQUILIBRIUM.

The affinity of Nitrogen for Hydrogen even at high temperatures or under the influence of the electric spark is very slight. Various catalyzers will increase the velocity of the reaction somewhat, but even the best of these produce only a fraction of a percent of ammonia if the reaction proceeds under atmospheric pressure. The reaction, $N_2 + 3H_2 = 2NH_3$, is an exothermic one, about 10,070 calories being evolved for every gram molecule of ammonia formed. This fact at first sight might lead one to predict that the two gases would unite quite readily, but a consideration of the other factors involved explains somewhat the small yields of ammonia actually obtained.

The first of these is the great inactivity of the nitrogen molecule at ordinary temperatures. Nitrogen can not be termed an inactive element as it forms a great number of compounds with other elements. In fact nitrogen in the atomic state must be classed as one of the most active elements known, and ^{it} is probably due to this great activity that a molecule of N₂ once formed is so hard to disrupt. Most of the elements which are gases have molecules made up of two atoms, but in none of them do the valences of the atoms seem to be so thoroughly satisfied as in the case of nitrogen. Nitrogen as a gas will unite with practically no other simple element or compound below a temperature of 300 C. Around this temperature it will form fairly readily nitrides of the alkaline earth metals or their carbides. From this alone it can be seen that the problem of effecting the combination of nitrogen and hydrogen is a difficult one.

Another factor which retards the union of the two gases is the rather complex molecule formed. If the reaction is considered from the standpoint of the kinetic molecular hypothesis, it is evident that the formation of a molecule of NH₃ requires the collision of three hydrogen atoms with one of nitrogen, which would occur infrequently as compared to the collision and consequent reformation of molecules of N₂ and H₂.

From the above statement it is evident that to effect combination the gases must first be ionized either by using high temperatures or by the electric discharge. And since the influence which effects ionization is equally as effective in disrupting the molecules, a small yield of ammonia is to be expected. This is borne out experimentally by the fact that a mixture of the two gases subjected to prolonged treatment with the electric spark or silent discharge are on analysis found to contain only about three per cent of ammonia. In other words, assuming the ionization to be 100 per cent, 97 per cent of the total number of atoms recombine to form H_2 and N_2 respectively, while three per cent have united to produce ammonia. If the molecule formed was NH or even NH_2 , it seems highly probable that much greater yields could be attained.

In commercial work the only practicable way to effect ionization is by the use of high temperatures, but their use interposes still another obstacle to the formation of the desired compound. From the equilibrium, $N_2 + 3H_2 \rightleftharpoons 2NH_3$, it can be seen that one volume of nitrogen combines with three of hydrogen to form two of ammonia or four volumes combine to form two. It is therefore apparent that by increasing the pressure the equilibrium can be shifted to the right or in the direction of more ammonia produced. Conversely decreasing the pressure decreases the amount of ammonia formed. This fact affects the problem vitally for in heating the gases, unless they are held under pressure, a rarefaction of the gases occurs in accordance with the law of Henry (the volume varies as the absolute temperature if the pressure remains constant) which is in effect decreasing the pressure. Since the ionization does not begin to be appreciable until a temperature of around $500^\circ C$ is reached, it is to be expected that at this temperature the amount of ammonia produced at atmospheric pressure will be considerably smaller than at ordinary temperatures and using other means of ionization.

This can readily be seen by referring to the following table of the amounts of ammonia in equilibrium with nitrogen and hydrogen at different temperatures and pressures as given by Haber:

Temperature	Per cent of ammonia in equilibrium		
	1 Atmosphere	100 Atmos.	200 Atmos.
200°C	15.3	80.6	85.8
300	2.18	52.1	62.8
400	.44	25.1	36.3
500	.129	10.4	17.6
600	.049	4.47	8 .25
700	.0223	2.14	4.11

From the table it can be seen that the lower the temperature the greater the amount of ammonia in equilibrium. But in the synthesis of the gas from nitrogen and hydrogen there must also be taken into account the rapid decrease in the reaction velocity with the temperature, and since at values much below 500° the reaction velocity becomes impracticably small, even with the use of a catalyzer, a lower limit to the temperature is arbitrarily fixed, thereby. Experiments run using no catalyzer showed no measurable amount of ammonia formed below 550°.

The above values give the percentage of ammonia in equilibrium with nitrogen and hydrogen for different temperatures. These values are not easily reached experimentally, especially those for lower temperatures. If ammonia gas is heated up to 1000° the disassociation into nitrogen and hydrogen is practically complete. For temperatures below 1000° if ammonia gas and a mixture of nitrogen and hydrogen are heated to the same temperature it will be found that a catalyzer must be used or a long time allowed to elapse before the amounts of ammonia in equilibrium in both cases become the same. This is particularly true for values below 550 . There will be considerable discrepancy between the amount of ammonia formed by heating the gas mixture and the amount of ammonia remaining undecomposed, so that for lower temperatures the equilibrium point is perhaps best calculated from thermodynamical considerations.

Having now discussed the factors which affect the equilibrium, it is possible to consider means which might be taken to increase the amount of NH_3 produced. The first and most obvious method, i. e. that of increasing the pressure, is taken advantage of in the Haber process, pressures as high as 200 atmospheres being used.

The next most obvious point of attack is the catalyzer used. Recognizing the importance of the catalytic function many investigations have been made into the relative efficiencies of various materials and the effect of extraneous bodies on their activity. The most favorable catalysts are metallic osmium and uranium carbide. The former is much too rare and costly for ordinary use while the latter suffers from the disability that it is decomposed by the very slightest traces of moisture, rendering necessary a most rigorous desiccation of the gases. The common contact substance used is iron. It is prepared by reducing the oxide in a current of hydrogen at high temperatures, some sort of a carrier such as pumice usually being added. Another method of preparation is by heating a complex organic salt of iron such as the citrate, tartrate, oxalate, ferrocyanide, etc., driving off the carbon and hydrogen as CO_2 and H_2O leaving the iron in a finely divided condition.

It has been found that just as small traces of some materials will "poison" the catalyst and render it ineffective, so there are certain other substances, so called promoters, which increase the activity of the catalyst markedly. As in the case of poisoners, only minute traces of such substances are required. Chief among these are salts of the alkalies and the cyanides of the alkaline earth metals. Just how these promoters assist in the process is a matter of considerable doubt, and will be discussed more fully under the general theory of catalysis.

So far no catalyst has been found which is active below a temperature of 500. However, granted the possession of a catalyzer quite active at this temperature, reference to the table will show

that high pressures are necessary to obtain anything like a satisfactory yield of NH_3 . If a catalyzer were known which would function readily below 500° or if conditions could be altered so as to render already known contact substances active at lower temperatures, a very small lowering of the temperature would effect a comparatively large increase in yield as the percentage of ammonia in equilibrium increases rapidly below 500° .

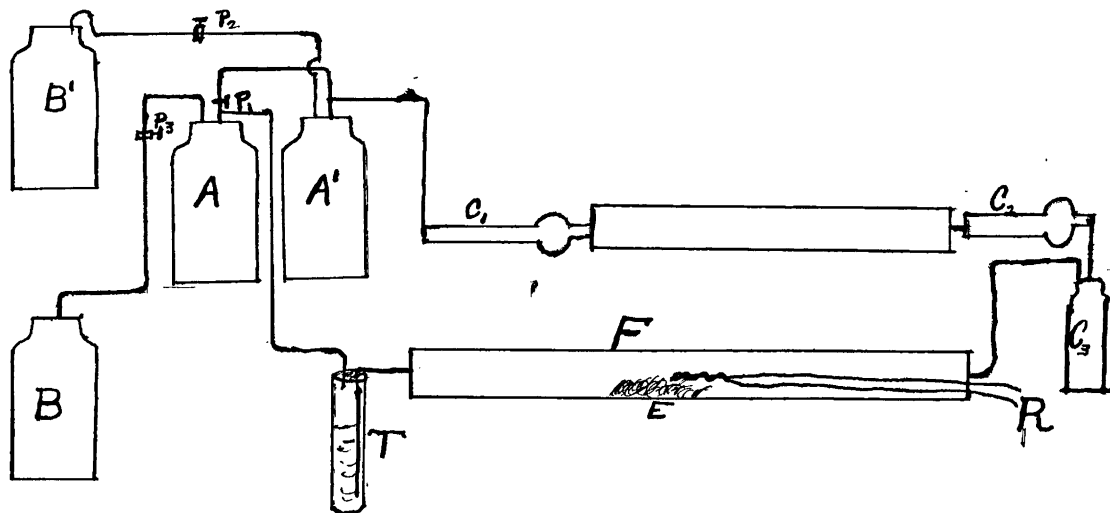
THEORY OF THE CATALYTIC FUNCTION.

Two main theories have been advanced to explain the manner in which the catalysts used increase the velocity of the reaction. These are the intermediate compound theory and the surface energy or adsorption theory.

The intermediate compound theory, which is the one most generally held in this particular reaction, postulates the interaction of the iron and nitrogen at the high temperatures employed to form a nitride of iron. This on breaking down gives up its nitrogen in a nascent or atomic state, whereupon it unites readily with the hydrogen to form NH_3 . An argument for this theory is that most metallic nitrides when heated in an atmosphere of hydrogen will give up their nitrogen as ammonia. However, there are several arguments against this theory. One is that there seems to be considerable uncertainty as to the composition of iron nitride. Some of the formulas given are Fe_2N , FeN , Fe_3N_2 and Fe_5N_2 . It seems probable that some of these so called compounds contain occluded nitrogen. Another consideration is that under constant conditions of temperature and pressure and definite proportions of nitrogen and hydrogen in the surrounding gas mixture a state of equilibrium between the nitride, nitrogen and hydrogen should be reached instead of a condition of alternate formation and decomposition as pictured by the theory. If a nitride really is formed, then by passing nitrogen and hydrogen alternately over the heated catalyst a much better yield should be obtained. This has been found to be the case, but the increase is not nearly so marked as one might expect. This fact makes the increase in yield an equally good argument for the surface energy theory.

This theory assumes that the action of the catalyst is due to the surface energy which it is well known exists between the surfaces of finely divided metals and gases surrounding them. Nearly all metals in a finely divided condition will take up varying amounts of different gases. Well known examples of this are platinum and paladium which take up or occlude large quantities of hydrogen. It has been proven that in such cases no definite chemical compound is formed. Therefore, since the amount of gas taken up varies as the available surface of the occluding metal, it seems probable that there is a concentration of the gas on the surface of the metal, in which condition the molecules of the gas are brought into much closer juxtaposition with one another. Applying this to the problem under consideration, the action of the catalyst may be considered due to the fact that the atoms of nitrogen and hydrogen are literally forced together by being condensed on the surface of the contact body. The experimental work carried out seems to indicate that surface energy does play an important part in the catalytic function. This does not conflict with theory since if iron does form a nitride, it is most likely that a strong attraction exists between the metal and the gas molecules. At lower temperatures the gas is merely adsorbed on the surface and the mass is not strictly homogenous. When, however, the temperature is raised to the critical point, the attraction between the iron and nitrogen still persisting, the mass assumes molecular homogeneity or in other words becomes a compound. Some of the experiments carried out show conclusively that adsorption plays a part in the action of the catalyst. When the furnace was allowed to cool down and the catalyst removed and heated again in air a considerable amount of ammonia was evolved. This is explained by the fact that the nitrogen and hydrogen adsorbed on the surface of the contact body united to form ammonia which was also adsorbed, and since the amount of gas which any substance is capable of adsorbing varies inversely as the temperature, heating up the mass caused the evolution of NH_3 along with some nitrogen and hydrogen.

DESCRIPTION OF THE APPARATUS.



A' was a two liter bottle which was filled with a mixture of three parts of hydrogen to one of nitrogen. By opening pinch cocks P_1 and P_2 the gases were forced first thru the calcium chloride drying tube C, and then through the small furnace D which consisted of a quartz tube $3/4$ " in diameter wound with resistance wire and heated to a temperature of 500° . The purpose of this furnace was to take out any oxygen which might be present in the gases by causing it to combine with the hydrogen to form water. The water vapor thus formed was removed by drying tube C_1 and by the sulphuric acid drying bottle C_3 , which also removed any traces of NH_3 formed in the furnace. R was a pyrometer which extended into the furnace near the catalyst, thus giving the temperature of the latter at any time. On leaving the sulphuric acid drying bottle the gases passed next through the main furnace F, a tube about 1" in diameter which could be heated to any desired temperature by a resistance coil around it, the gases passing over the catalyst and through the tube T which contained N/20 sulphuric acid. In this way any ammonia formed in the furnace could be accurately measured. The uncombined gases then passed into the bottle A displacing the water with which it was filled into B. By opening pinch cock P_1 and changing the position of B' and B the gas could be forced back into A' again and so on through the system.

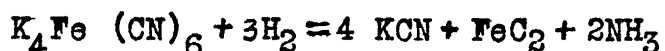
PROCEDURE.

The general method of procedure was as follows:

The gas mixture was passed through the system as outlined above, with no catalyst in the large furnace F. Runs were made at different temperatures, beginning at 450° and increasing by 50 degree increments up to 650. It was found that the amount of NH₃ formed below 550° was so small that it could not be detected by the method used, which was sensitive to at least .00005 grams or to about .001%. It was early noticed that the amount of NH₃ formed, other things being equal, depended on the rate at which the gases were forced through the furnace, the slower the rate of flow, the larger the percentage of ammonia formed. To facilitate comparison all runs were made using a rate of flow of approximately one liter every 15 minutes.

TEMPERATURE	USING NO CATALYST. %NH ₃ FORMED	% NH ₃ IN EQUILIBRIUM (HABER)
450	.000	.440
500	.000	.129
550	.001	.077
600	.0064	.049
650	.0082	.032

A catalyzer, prepared by reducing Fe₂O₃ with hydrogen using pumice as a carrier was then placed in the furnace and runs made as before. The results secured, however, were unsatisfactory and this catalyst was discarded for one made by heating potassium ferrocyanide in a current of hydrogen at about 400°. Just how this salt acts when so treated is not known definitely, but it is certain that NH₃ and KCN are among the products formed. The reaction probably goes as follows:



The catalyst so formed seems to be one of the most efficient so far discovered, very high yields being claimed for it in the two patents covering its preparation and use.

As before mentioned KCN is one of the substances which act as a promoter for catalysts used in the production of synthetic ammonia. In addition to this, since the molecule has just given up ammonia it seems likely that its molecular structure should be such as to make it particularly efficient as a catalyst. In using the above it was found necessary to heat for a long period in order to be certain that no error resulted from the ammonia produced by the decomposition of the catalyst.

USING THE POTASSIUM FERROCYANIDE CATALYZER		
TEMPERATURE	% NH ₃ FORMED	% NH ₃ IN EQUILIBRIUM
350	.000	1.31
400	.001	.44
450	.012	.285
500	.017	.129
550	.021	.077
600	.0295	.032

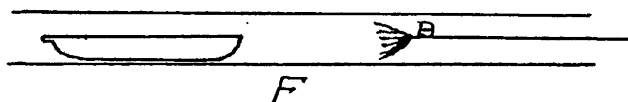
The above values are the average produced by a series of runs using this catalyzer which deteriorated considerably towards the last. Heating up and cooling down of the contact body seems to have a deleterious effect as does handling and exposure to the air, particularly the latter since it seems to be hygroscopic due possibly to the carbide present.

EFFECTS PRODUCED BY USING AN ELECTRICAL DISCHARGE.

An attempt was next made to use a combination of electric discharge with a catalyst in order to determine what effect, if any, ionization of the gases has on the action of the contact body. Theoretically a number of things might be expected to happen. (1) Assuming that the ionization of the gases has no effect on the activity of the catalyst, a larger production of ammonia should result for some NH₃ should be produced from the gases by the discharge alone, in addition to that formed by the catalyzer, unless the ammonia formed by the discharge was in some way decomposed by the contact body which seems very unlikely. (2) In addition one would predict that

if the action of the catalyst is due to the close contact brought about by condensation of the gases on the surface of the catalyst that previous ionization of the gases would facilitate their union to produce ammonia. This of course assumes that the preferential adsorption of the gases by the catalyst will not be lessened by ionization. By making the contact body the cathode the tendency for the ionized particles to be adsorbed should be greatly increased since they are positively charged. (3) It can easily be shown experimentally that there is a considerable difference of potential between two bodies when a state of tension exists at the surface interface. Glass and water and oil on water are good examples of this. A difference of potential sometimes as high as five volts exists between water and a layer of oil on its surface. Therefore, it seems possible that if a large difference of potential was created between the catalyst and surrounding objects that it might exert some influence on the amount of gas adsorbed by the contact body.

APPARATUS USING COMBINED ELECTRIC DISCHARGE & CATALYST.



The apparatus was then arranged as shown above. The catalyst prepared from the ferrocyanide was placed in a small porcelain boat which was connected by a wire with the negative pole of a large induction coil. B was a brush made of small iron wire which was connected to the positive terminal of the coil. A number of runs were first made using an aluminum disk in place of the porcelain boat in order to determine the amount of ammonia formed by the discharge. It was found, however, that for temperatures over 350° a good discharge could not be obtained as above this temperature glass, porcelain or quartz all become good conductors so that the current was carried by the containing tube

with

rather than by the gases between the two terminals. The result was that the ionization alone was not sufficient to produce a detectable trace of ammonia. This difficulty was never satisfactorily overcome. The first runs were made using aluminum wire in the place of iron, but it was found that the aluminum deposited on the contact body and acted as a poisoner. Using iron wire overcame this objection since the finely divided iron produced is itself an active catalyzer. The procedure followed was to make a run using no discharge, titrate the amount of ammonia thus formed, and then holding the temperature and other conditions as nearly constant as possible repeat the run using a discharge between the terminals. The first runs thus made showed a considerable increase in the amount of ammonia produced. The difference between the yields, however, decreased quite rapidly due probably to the deposition of metal on the sides of the tube and the consequent cutting down of the effectiveness of the discharge. Some of the results obtained are given in the following table:

USING DISCHARGE WITH CATALYZER.		
TEMPERATURE	WITHOUT DISCHARGE	WITH DISCHARGE
450	.0135%	.0432%
500	.0182	.0273
550	.0214	.0266

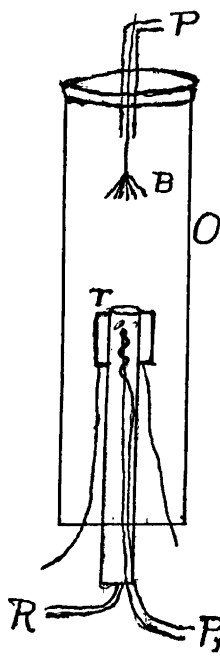
The first run made showed a very large increase in yield obtained with the discharge compared to that formed by the catalyst alone. However, check results could not be obtained on any of these values. The steady decrease in yield obtained with the discharge at increasing temperatures was due probably not to the rise in temperature but to the decreasing efficiency of the discharge produced by short-circuiting through the walls of the furnace. The catalyst was also found to deteriorate more rapidly when the discharge was used.

The possibility as mentioned under (3), that the difference in potential between the contact body and surrounding objects might have some effect on the adsorption, did not seem to be borne

out. No particularly accurate attempt was made to check up on this however. The furnace with the catalyst in it was heated up after cooling down from a previous run, the ammonia evolved in the furnace from heating up the catalyst was neutralized in the acid solution by sweeping more gas through the furnace, and then holding the temperature constant the discharge was run for a few seconds using the catalyst as both anode and cathode. In neither case was there sufficient ammonia evolved to be detected. This was found to be true for all temperatures from 100 to 550°.

Even if the difference of potential did affect the adsorb-^{tion} materially, it is unlikely that there would be any great difference in the amounts of ammonia produced, since during runs either with or without the discharge the potential of the contact mass remains constant. Difference in the degree of adsorb^{tion} alone would not increase the yield. If however it is true that the degree of adsorb^{tion} is varied by differences of potential, then rapidly changing the potential should increase the amount of ammonia produced.

In an attempt to overcome the difficulty caused by the walls of the small furnace becoming conducting at high temperatures a new furnace was constructed as shown by the diagram.



The larger outer portion O was a piece of glass tubing 4" in diameter, the top of which was closed with a large rubber stopper paraffined in. B was a brush of small iron wire as before suspended directly over the porcelain tube T which was wound with resistance wire at the upper end and this in turn covered with heat insulating material. The catalyzer was placed in the upper end of this tube surrounding the pyrometer. The gas entered at P, passed down over the brush B where it was subjected to the ionizing effect of the discharge before passing over the catalyzer in the upper end of the tube. The gases left the furnace at R and were handled with the same apparatus as in the previous furnace. Satisfactory results were not secured with this

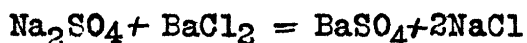
apparatus due chiefly to the fact that the radiation was so great that the catalyst could not be heated evenly, particularly the upper portion of it which was the part first exposed to the cold gases. A very slight increase in yield was evident when the discharge was used. The total amount formed in either case, however, was very much smaller than in the other furnace, due as before stated to poor distribution of the heat through the catalyst and the gases.

RESULTS PRECIPITATING AMMONIA AS NH_4Cl and $(\text{NH}_4)_2\text{CO}_3$.

An attempt was made to attack the problem from still another side. The reaction $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ is of course an equilibrium one, but the amount of NH_3 in equilibrium with N and H at temperatures necessary to the production of ammonia is very small. The equation is analogous in some respects to the following:



where a certain amount of NaBr exists in equilibrium with NaCl, KBr and KCl. Considering the equation



we know that it goes to completion due to the fact that barium sulphate is practically insoluble which means that Ba ion and SO_4 ion once united to form BaSO_4 are immediately removed from the system. The mass law states that the speed of a reaction is proportional to the molecular concentration of the reacting substances. In this case the concentration of Ba and SO_4 ion on the right hand side is practically nil at all times, hence the reaction proceeds rapidly to the right to completion. If a third substance such as HCl were introduced into the equation $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ we would have $\text{N}_2 + 3\text{H}_2 + 2\text{HCl} = 2\text{NH}_4\text{Cl}$ - - the product on the right, ammonium chloride is a solid, and the reaction might be expected to go to completion since due to the attraction of gravity the ammonium chloride should fall from the sphere of reaction.

An experiment was arranged as follows:



P and P' were two plates placed about 3/8" apart and connected to the two terminals of an induction coil. The bottle was filled with HCl, N and H in the theoretical proportions

to form NH_4Cl . Thus the NH_3 formed by the silent discharge ought immediately to react with the HCl and be precipitated as ammonium chloride. A small amount was obtained in this way, but it fell far short of what theoretically should have been produced if the figures given by Davies^r are correct. The small yield may be explained by the fact that a molecule of NH_4Cl once formed is so small that its motion due to the attraction of gravity is very slow, and only when it forms an agglomeration with other similiar molecules does it fall with appreciable velocity. In the meantime it is within^s the sphere of electrical activity and the NH_4Cl molecule is likely to be again disrupted much as would a molecule of NH_3 . In addition since the HCl is broken up by the discharge there is the reverse reaction $2\text{NH}_3 + 3\text{Cl}_2 \rightleftharpoons \text{N}_2 + 6\text{HCl}$.² This latter however is not sufficient to explain the small yields secured. No better success was obtained using CO_2 and water vapor in an attempt to precipitate $(\text{NH}_4)_2\text{CO}_3$. The working out of the above reactions quantitatively should prove very interesting as there is apparently nothing in the literature concerning them.

SUMMARY.

(1) Ionization of the gases before reaching the catalyst will produce an appreciable increase in the amount of ammonia over the sum of that produced by using the discharge and the catalyst separately. It is probable that this increase is due either to the increased adsorbing power of the catalyst for the ionized gases or to the fact that the ionized gases once adsorbed react with greater readiness than do unionized molecules.

(2) Changing the potential of the contact mass apparently has no effect on the degree of adsorbtion.

(3) Attempts to precipitate reaction products as solids from a reaction between gases where the reaction goes on under the influence of an electric discharge show that the yields fall far short of the theoretical amount.

(4) The catalysts used in the synthesis of NH_3 from N and H seem to function by adsorbtion of the gases rather than by the formation of an intermediate nitride.

1 & 2 from pg. 14.

1. Zeit. Phys. Chem 64, 657, 1908
2. Jour. Am. Chem. Soc. 905, May, 1917.

REFERENCES.

- Zeit. Angew. Chemie 27, I, 473 (1914)
Science, 40, 899-903 (1914)
General Elec. Review 18, 1042 (1915)
Trans. Am. Inst. Elec. Engineers 34, 2646 (1915)