The History of the Catalytic Synthesis of Ammonia

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1. Driving Forces for the Fixation of Atmospheric Nitrogen

In September 1898, in his presidential address to the British Association for the Advancement of Science, Sir William Crookes [1] warned that

> "*England and all civilised nations stand in deadly peril of not having enough to eat.*"

He had arrived at this disturbing conclusion after a critical examination of the area of arable land available for wheat growing, and the rate of increase of the wheat-eating population, which showed that

> "*our wheat producing soil is totally unequal to the strain put upon it.*"

Having brought attention to the possibility of future famine, however, he then pointed the way to a possible solution to the problem, using the following prophetic words:

> "*It is the chemist who must come to the rescue of the threatened communities. It is through the laboratory that starvation may ultimately be turned into plenty. Before we are in the grip of actual dearth the chemist will step in and postpone the day of famine to so distant a period that we and our sons and grandsons may legitimately live without undue solicitude for the future.*"

What evidence was there for Crookes' optimism?

It was recognised, at that time, that certain materials improved the yields of agricultural crops. John Bennet Lawes had carried out extensive experimentation on his estate at Rothamstead, during the mid nineteenth century, investigating the requirements of various crops, and, with Sir Henry Gilbert, had demonstrated that the application of nitrogenous fertiliser to wheat crops greatly improved the yield per acre of soil. Thus, wheat supplies could be ensured, provided a reliable source of nitrogenous fertiliser was available.

At that time the principal sources of such 'fixed' nitrogen compounds were threefold. Ammonium sulphate was produced during the distillation of coal, but amounts were not great. Guano deposits, off the coast of South America, had also been worked, but were coming close to exhaustion. The major source was situated in the rainless districts of Chile, where large nitrate beds had assumed vast commercial importance. It was considered unlikely, at that time, that any similar such nitrate deposits would be discovered elsewhere in the world, because, owing to its great solubility, sodium nitrate can only accumulate in areas of little rainfall. Contemporary estimates of the reserves of Chilean nitrate indicated that they would reach exhaustion 50 years from the date of Crookes' address if the usage was maintained at the prevailing level, but would run out much sooner if the fertiliser application rate were to increase commensurately with the rate of increase of population growth. Thus, while the application of nitrogenous fertiliser to the soil could provide a temporary respite to the problem of food supply, there appeared to be no escape from the ultimate fate the exhaustion of nitrate reserves would bring. There was, however, one ray of hope amidst all this gloom: although the natural reserves of fixed nitrogen were finite, the reserves of free atmospheric nitrogen are vast. If a method could be found of fixing this atmospheric nitrogen into a form more useful as fertiliser, the problem of food supply would be solved. This led Crookes to declare that

> "*the fixation of atmospheric nitrogen is one the great discoveries awaiting the ingenuity of chemists.*"

Up until 1900, numerous attempts had been made to fix atmospheric nitrogen. Some of these attempts had been successful to a degree, but none had converted more than a small amount, and at a cost largely in excess of the corresponding market value of fixed nitrogen. In 1892, Crookes himself had demonstrated the fixation of atmospheric nitrogen in a lecture entitled "The Flame of Burning Nitrogen", in which, by the passage of a strong induction current between terminals "the air takes fire and continues to burn with a powerful flame, producing nitrous and nitric acids." The first atmospheric nitrogen fixation process to be successfully developed commercially, the Birkeland-Eyde process, was based on this observation by Crookes. The direct combination of nitrogen and oxygen of the air was effected by means of an electric arc; the very high temperatures required to form nitric oxide (greater than 3300 K) could be attained only by its use, and thus vast quantities of energy were needed. A yield of only 2 per cent nitric oxide in the effluent gas was achievable and the large excess of air which remained uncombined had also to be heated up, thus only 3–4 per cent of the electrical energy consumed was actually used to unite nitrogen and oxygen. Consequently, the process was only viable in places where electric power was cheap, the first fullscale plant being set up in Norway in 1905. The Badische Anilin and Soda Fabrik of Germany were also interested in the electric arc method and had been studying the reaction since 1897. In 1904 they published a patent which claimed to produce a steadier arc than that of the the Norwegians, and in 1906 a joint Norwegian/German venture was set up using BASF's furnace. BASF withdrew five years later, being more interested in another method of nitrogen fixation which will be described later.

An alternative process of nitrogen fixation had been based on the observation by Frank and Caro in 1898 that a mixture of barium cyanide and barium cyanamide could be obtained when barium carbide was heated, at high temperature, in a nitrogen atmosphere. It was later discovered that calcium cyanamide could similarly be obtained by heating calcium carbide with nitrogen at 1500 K, and the cyanamide compound thus formed could be used directly as a fertiliser. Ammonia could also be obtained from the cyanamide by hydrolysis. One advantage of this process over the arc process was that, once the reaction of calcium carbide with nitrogen had begun, the electric power could be disconnected, the exothermic reaction being self-sustaining. The initial production of calcium carbide, by heating calcium oxide with carbon, did, however, require temperatures of 2300 K. The overall power requirement was only a quarter of that of the arc process, and considerable development of the cyanamide process occurred in Europe, successful plant operation being achieved by 1910.

Although both the arc and cyanamide processes did assume some commercial importance, they were eventually to be displaced by another method of nitrogen fixation, which did not suffer the disadvantage of requiring extremely high temperatures. This new process achieved commercial viability in 1913, and was destined to become one of the most significant developments in industrial chemistry. This process was the catalytic synthesis of ammonia from its elements, pioneered in Germany by Fritz Haber and his research group at Karlsruhe and developed to industrial scale by Carl Bosch at the Badische Anilin and Soda Fabrik in Ludwigshafen. In this process, the combination of nitrogen with hydrogen was effected at temperatures of around 820 K, by means of an iron catalyst, and since the reaction was exothermic, once started it did not require further heat input. Up until 1912, general opinion seemed to agree that the future expansion of the fixed nitrogen industry lay with the further development of the arc and cyanamide processes, the 'Haber process' merely warranting occasional mention in the literature of the time. In fact, an extensive programme of work had been carried out by BASF in Germany, with the ultimate aim of perfecting the Haber process, but the details of this work, for obvious commercial reasons, had been kept largely secret. Events of the next few years were to have an important effect on the further development of the process.

Although the commercial production of fertiliser was undoubtedly the primary aim behind all efforts to fix atmospheric nitrogen, there arose, in addition, another driving force. Nitrates were essential for the manufacture of conventional explosives of military value, and an adequate supply was essential to any type of military programme.

At the outbreak of the First World War, the major source of nitrates was still in Chile, and it became obvious that any belligerent country that was effectively cut off from these supplies would be at a grave disadvantage. During the war, the German authorities supported the development of a nitrogen fixation programme, with the aim of ensuring independence from Chilean nitrates. Both the cyanamide and Haber processes received government support, and further development of the Ostwald process, which effected the oxidation of ammonia to nitric oxide, which could subsequently be converted to nitric acid, was also encouraged. It was reported at the time that it was highly likely that the war would have ended in 1916, but for the existence of the Haber process.

2. Haber's Work on the Synthesis of Ammonia

A. Initial Involvement of Fritz Haber [2, 3]

Fritz Haber first became interested in the fixation of atmospheric nitrogen when visiting the United States in 1902 on a fact-finding mission on behalf of the Bunsen Society to observe the technical and educational progress of that country. He visited the establishment of the Atmospheric Products Company, at Niagara Falls, at which the arc process was being operated.

Plate 1. Fritz Haber. (Reproduced with permission from "Geschichte der Ammoniaksynthese", A. Mittasch, (1951), Verlag Chemie, facing p 65)

He reported that, in spite of the importance of the undertaking, the degree of development was disappointing, the installation being more of an experimental apparatus than an industrial operation. On his return, Haber carried out his own investigations, supported by BASF, on the formation of nitric oxide and was granted German and British patents in 1907, for "the production of compounds of nitrogen and oxygen by subjecting such air or mixture to the action of an electric arc". Although this work showed some promise in commercial application it was to be far outweighed in in importance by his later accomplishments. The beginnings of his involvement in the attempts to synthesise ammonia from hydrogen and nitrogen occurred in 1903, when the Margulies Brothers of the Austrian Chemical Works in Vienna asked him to assist them in their work. They had been engaged in attempting to synthesise ammonia by the action of hydrogen on the nitrides of calcium, lithium and magnesium, but had only obtained trivial amounts up to that point.

Haber was then 35 years old and was a professor at the Technische Hochschule in Karlsruhe. He had achieved certain recognition up to that time, as evidenced by his selection as representative of the Bunsen Society to visit the U.S.A., but he was essentially still an ambitious man who was anxious for success. His earlier career had been a curious mixture of failure and disappointment. He was born into a prosperous family with a chemical tradition, his father, Siegfried, being owner of an established pigments and dyestuffs merchandising company in Breslau, which was one of Germany's largest importers of natural indigo. His mother, Paula, did not survive the birth of her son, who was therefore brought up by a series of relatives until his father's second marriage. His childhood was, nevertheless, a happy one, and he was encouraged in his school studies becoming well-acquainted with literature, classics, drama and philosophy, although by tradition little science was taught at that time. When almost eighteen he began his studies at the University of Berlin, where he developed an interest in chemistry which was fuelled by various factors. Ability in chemistry would be of obvious assistance in his father's business. Also, at that time Germany was the centre of world expertise in chemistry, and to be a German chemist was to be a member of a prestigious profession.

Haber studied at Berlin under Professors Helmholz and Hoffmann, the former codiscoverer of the first law of thermodynamics, the latter discoverer of aniline and founder of the coal-tar industry. Following the tradition of the time, after a year at Berlin Haber moved on to the University of Heidelberg, where he studied under Professor Bunsen.

After Heidelberg, Haber returned home to Breslau in order to serve his compulsory year of military training, which passed enjoyably, especially the academic lectures on philosophy, and in 1889 he enrolled at the Charlottenburg Technische Hochschule, the largest engineering college in Germany. It was here that he carried out his first research work, under the guidance of Karl Liebermann, one of the cosynthesisers of alazarin dye. In 1891 he received his doctorate for work related to piperonal, but did not distinguish himself in his final exam. Having spent some time with organic synthesis, Haber's next goal was to study with Wilhelm Ostwald at Leipzig, but his hopes were dashed when Ostwald turned him down. Consequently he sought work in the chemical industry but had to go to Budapest to find it. This position, in a distillery, lasted a year but was totally without distinction as were subsequent appointments in a fertiliser factory and a textile company, which involved purely clerical work. In 1892 he returned to the study of chemistry, this time in Switzerland at the Federal Polytechnic School in Zurich, where he studied physical science and technology under Professor Lunge, and then, aged 24, he returned to work for his father, whilst waiting for a suitable employment opportunity in the chemical industry. The association between father and son, however, was not successful, frequent arguments and disagreements being common, and a parting of the ways was inevitable. This took place in the summer of 1892. The two had disagreed about the importing of a chemical to treat a cholera epidemic. Siegfried had eventually accepted his son's judgement, but later, when it proved disastrous, he ordered his son out, declaring, "Go to a university. You don't belong in business!" [2].

Haber had reached a low spot in his career. His academic achievements had not been great, his industrial record still worse and his association with his father a disaster. A further unsatisfactory period at the University of Jena as assistant in Professor Knorr's laboratory followed before he finally achieved a satisfactory position at the Karlsruhe Technische Hochschule, as assistant in the Department of Chemical and Fuel Technology, under Professors Bunte and Engler. Here, under the guidance of Bunte, Haber carried out some work of substance. His first two years were taken up by a study of the pyrolysis of hydrocarbons, searching for a general rule for such decompositions; this work was one of the first investigations of the cracking process now used in the oil industry. He published his results in a volume entitled "Experimental Studies on the Decomposition and Combustion of Hydrocarbons" in 1896, the book was received well and he was accepted onto the faculty at Karlsruhe. Here, under the influence and direction of Hans Luggin, who had studied with Arrhenius, Haber developed a keen interest in physical chemistry, a discipline so far unknown to him. Investigations in the field of electrochemistry culminated in the publication, in 1898, of his book, "Outline of Technical Electrochemistry on a Theoretical Basis", which was unusual at the time in that it brought together theory and practice as a unified whole. Although not received with great enthusiasm by the German Electrochemical Society, the book was considered of great importance by other prominent physical chemists of the day and was a major reason for Haber's promotion to associate professor at Karlsruhe. Over the next few years, Haber devoted much time to the study of electrochemistry and gained prominence in the German Electrochemical Society, so that when approached by the Margulies brothers in 1902 he was already of some fame among physical chemists. The following year he published his famous book, "The Thermodynamics of Technical Gas Reactions", which was to have a profound influence on physical chemistry.

At Karlsruhe, Haber had acquired a reputation as an adept raconteur, with a particular liking for the classics. He had a prodigious capacity for work, often continuing late on into the night, completely immersed in a particular problem to the exclusion of all else. Above all, he was renowned for his ability as a critic, never failing to bring attention to errors made by others.

B. Early Attempts at the Synthesis of Ammonia

Haber agreed to help the Margulies Brothers, and in involving himself with the preparation of ammonia, had undertaken a task which had occupied many investigators for well over a century. Ammonia was first prepared in 1774, by Priestley [4], and since the first comprehension of its composition by Berthollet [5] in 1784, attempts to synthesise it from its elements had been numerous. In 1795, Hildebrandt [6] carried out the first attempts at a synthetic preparation, carrying out systematic and extensive experiments, but achieved no success. In 1823, Dobereiner [7] was the first to claim a successful catalytic combination of nitrogen and hydrogen. During numerous experiments on the combustion of gases, using platinum as catalyst, he reported that during the combination of hydrogen with the oxygen in the air "sufficient of the oxygen was not available to satisfy all the hydrogen, so the excess reacts with nitrogen to form ammonia." His conclusion was obviously incorrect, but as the experimental method was not explained, the source of his error cannot be ascertained.

In 1839, whilst undertaking experiments on the catalytic synthesis of ammonia, Kuhlmann [8] proposed the 'status nascendi' theory. He first tried to combine free hydrogen and nitrogen by means of platinum sponge or platinum black, but did not succeed. Further experiments were made with 'nascent' nitrogen, by passing nitric oxide and hydrogen over platinum sponge, and this time he claimed success. He made the following generalisation: "When hydrogen or hydrocarbons come into combination, under favourable conditions, with 'nascent' nitrogen, ammonia is formed". He also believed that, in the process of rusting, nitrogen of the air was bound with nascent hydrogen to form ammonia. There were notable critics of Kuhlmann's theory, but no less an authority than Liebig [9] supported Kuhlmann's views. In 1844, he reported "We know of no case where combination of elemental hydrogen and nitrogen could be accomplished. The free state is a hindrance to the combination, however, once the elements are 'fixed' the reaction may go in this direction. What combines by this reduction with hydrogen is not normal nitrogen gas, but nitrogen gas in the 'nascent' state".

Kuhlmann's ideas prevailed for many years, and exerted considerable influence on both academic and technical work. Numerous attempts were made to synthesise ammonia from hydrogen and nitrogen, by first changing the experimental conditions in such a way as to render one or other of the reacting species 'nascent'. In particular, easily-accessible means were sought by which hydrogen could be obtained in the nascent state and subsequently made to react using cheap, practicable reactions. No success was obtained, however, and the problem of the catalytic synthesis of ammonia from its elements began to appear hopeless.

Although the synthesis reaction had not been successfully achieved, it had long been known that the decomposition reaction could readily be effected, and it was the study of the decomposition of ammonia which gave clues to the reasons for the failure of attempts at synthesis. St-Claire Deville [10] showed that when ammonia was exposed to an electric spark in a closed tube, there always remained a small quantity undecomposed. In 1884, Ramsey and Young [11] studied the decomposition of ammonia in a hot porcelain tube. Again, the most significant result of this investigation was that, even at very high temperatures (1050 K), the decomposition was not complete. The possibility of the existence of an equilibrium position had been demonstrated.

The question of an equilibrium position was taken up by various investigators, some, notably, Ostwald [12], accepting its existence, others, such as Perman and Atkinson [13], claiming that their experimental results gave no evidence for such an equilibrium. At the turn of the century, however, the concept of chemical equilibrium, and the effects upon it of temperature and pressure, became clearer, due to the work of scientists such as Le Chatelier. The French chemist turned his attention to the position of the equilibrium between hydrogen, nitrogen and ammonia, at elevated pressure, where he had reasoned that the equilibrium concentration of ammonia should be more favourable. Unfortunately, this exercise terminated in a violent explosion, which killed one of his assistants; the project was abandoned, leaving only an obscure French patent [14], filed in the name of one of Le Chatelier's coworkers, to show for this effort.

C. Investigations on the Position of the Ammonia Equilibrium

1. Work of Haber and Van Oordt at Atmospheric Pressure [15]

The aim of the work carried out by Haber, in collaboration with the Austrians, was to achieve the continuous synthesis of ammonia by the simultaneous formation and reduction of a metallic nitride by the mixed gases, the metal phase acting as a catalyst. Haber decided first to determine the position of the equilibrium between hydrogen, nitrogen and ammonia as this would obviously govern the maximum yield of ammonia attainable. The first paper published by Haber on the formation of ammonia from its elements appeared in 1905, in collaboration with Gabriel van Oordt. In a series of what Haber later referred to as "fairly rough experiments", the position of the ammonia equilibrium in the region of 1300 K was determined. At a temperature of 1293 K, using pure iron as catalyst, the equilibrium position could easily be arrived at, from both the ammonia side and the hydrogen/nitrogen side. The results of the single experiments varied between 0.0052% and 0.012% ammonia, and originally Haber regarded the upper figure as the more likely value. The same results could be obtained with nickel, calcium and manganese as catalysts.

From the determination of the position of equilibrium at a single temperature, pressure and mixture of hydrogen and nitrogen, it was possible to predict, on the basis of theory, the approximate percentages of ammonia to be expected for any set of conditions. At that time, thermodynamics was becoming more and more useful to researchers concerned with equilibria. Van't Hoff, Gibbs and Helmholz had demonstrated the relation between heat of reaction, temperature and equilibrium constant, the application of which Haber was to elucidate in his famous book "Thermodynamics of Technical Gas Reactions" which appeared that same year. Van't Hoff's generalisation of the Clausius-Clapeyron equation allowed the calculation of the effect of temperature change on equilibrium from thermal data, and permitted the determination of the equilibrium constant at any set of conditions, provided it was already known for one set of conditions *i.e.*

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\Delta H}{RT^2}$$

where K is the equilibrium constant
T is the absolute temperature
R is the gas constant
ΔH is the heat of reaction

Haber used this equation to extrapolate the data obtained at 1300 K down to lower temperatures. Table 1 shows the results of these calculations taking the total pressure of the three gases as one atmosphere and the proportions of the hydrogen and nitrogen as stoichiometric; the table is based on the assumption that the upper value of 0.012% ammonia at 1293 K was the more likely figure. Haber concluded, from these figures, that the slight variations observed in temperature over the series of experiments were trivial compared with the error in the determination of the ammonia concentration, since the equilibrium varied only slowly with temperature. The more important conclusion, however, was his opinion that "from the beginning of red heat onwards, no catalyst can produce more than a trace of ammonia from the most favourable gas mixture if the experiment is conducted at normal pressure. Even at highly elevated pressures, the position of the equilibrium always remains very unfavourable. If one wishes to make ammonia successfully with a catalyst at normal pressure, one must not allow the temperature to go above 520 K. The uncertainty of the value used for the specific heat of ammonia, obtained by extrapolation, is, for the time being unavoidable, but it is inferred that the conclusions drawn will not essentially change, if a more precise figure for this quantity is ascertained in the future." It now became clear why many earlier investigators, who had generally worked at normal pressures and elevated temperatures, had failed in their attempts to synthesise ammonia.

At this point, in 1905, Haber regarded the further pursuit of the subject of the catalytic synthesis of ammonia from hydrogen and nitrogen as hopeless.

Table 1. Equilibrium data predicted by Haber and van Oordt. Based on their experimental results obtained at 1293 K and atmospheric pressure

	Composition of equilibrium mixture		
temperature/K	vol% H_2	vol% N_2	vol% NH_3
300	1.12	0.37	98.51
600	68.46	22.82	8.72
900	74.84	24.95	0.21
1200	75	25	0.024
1293	75	25	0.012

In the work with van Oordt, the preparation of ammonia from its elements had been demonstrated successfully, and the limiations to a synthetic route had been identified. At that time, Haber regarded the discovery of a catalyst which could bring the gases to equilibrium quickly at 570 K as unlikely, and also the commercial exploitation of a gas reaction at red heat under pressure as impossible, so the question of a technical-scale synthesis of ammonia was left dormant by Haber for the next three years.

2. *Work of Nernst at Elevated Pressure* [16]

Meanwhile, in 1906, Haber was obliged to consider a redetermination of the ammonia equilibrium to be necessary, because Professor Walther Nernst, of the University of Berlin, in the progress of his investigations on his 'Heat Theorem', had arrived at an approximation formula which could predict the position of equilibrium from the values of the heat of reaction and the so-called 'chemical constants'. As stated previously, Van't Hoff's generalisation of the Clausius Clapeyron equation allowed the calculation of the effect of temperature change on equilibrium from thermal data, but failed to give values of the equilibrium constant unless one value was already known experimentally for one set of conditions. Thus the integration constant had to be known before values of the equilibrium constant could be generated. This obstacle was overcome when Nernst arrived at the Third Law of Thermodynamics, which was then known as the Nernst Heat Theorem. With this concept, it was possible to calculate the chemical equilibrium for a given system from a few physical constants. Nernst used the new theorem to predict the positions of equilibria in various reactions, and, in many cases, found good agreement between his predictions and experimental results. This was not so in the case of the ammonia equilibrium. According to the Heat Theorem, Haber's results were incorrect. Nernst and his students set about establishing their own experimental data, conducting experiments at elevated pressures (50–75 atmospheres), and so becoming the first experimenters to synthesise ammonia at pressure. They obtained data which agreed with Nernst's predictions, but not with Haber's figures.

Table 2. Nernst's data for the ammonia equilibrium at normal pressure. Extrapolated from the experimental results obtained at elevated pressure

temperature/K	% NH_3 at equilibrium (observed)	% NH_3 at equilibrium (predicted by heat theorem)
958	0.0178	0.0196
1082	0.0087	0.0082
1109	0.0072	0.00702
1149	0.0055	0.00561
1193	0.0043	0.00448
1273	0.0032	0.00308
1313	0.0026	0.00261

(*c.f.* Haber and Van Oordt's figure of 0.0120% at 1293 K)

A comparison of the two sets of data is shown in Table 2. Nernst communicated the results of his experiments to Haber, by letter in 1906. The paper containing these results [16] was not due to appear until the meeting of the Bunsen Society in the summer of the following year. Meanwhile, Haber, in collaboration with Robert Le Rossignol, an extremely able experimentalist from England, who had studied in the laboratory of Sir William Ramsey, repeated the earlier determinations at normal pressure "paying more attention to detail than before".

3. *Work of Haber and Le Rossignol at Atmospheric Pressure* [17]

The new experiments of Haber and Le Rossignol were carried out using the earlier method of Haber and van Oordt, but employing a greater number of catalysts, various different reactor materials, a refined method for the determination of ammonia, and an improved apparatus; in particular, the measurements covered a temperature range between 970 and 1270 K. Much better reproducibility was observed in the later experiments. Nernst's equilibrium ammonia figures had been about a quarter of those of Haber and van Oordt. The later experiments of Haber and Le Rossignol showed that the equilibrium values lay at the lower limit of the band originally quoted by Haber and van Oordt, and not at the upper limit as they had originally thought. The higher figures were later ascribed to a particular property of the catalyst in the fresh state. Haber and Le Rossignol's newer figures, obtained at atmospheric pressure, were then as shown in Table 3, together with the calculated figures of Nernst using physical data available at the time. The discrepancy between the Berlin and Karlsruhe results was now somewhat smaller, Haber's figures being now only 3/2 times those of Nernst.

Although Haber had been obliged to modify his earlier views on the exact position of the ammonia equilibrium, he was now convinced that the experimental results obtained in collaboration with Le Rossignol more accurately reflected the true equilibria positions than did those of Nernst. He considered that, since Nernst had not studied the decomposition of ammonia in addition to the synthesis, it was questionable whether the equilibrium position had been achieved. Haber did, however, concede that the calculations carried out by Nernst would predict what Haber considered

Table 3. Haber and Le Rossignol's experimental data for the ammonia equilibrium at normal pressure

temperature/K	% NH_3 at equilibrium
973	0.0221
1023	0.0152
1123	0.0091
1203	0.0065
1273	0.0048

(*c.f.* Nernst's figure of 0.0032% at 1273 K) to be the correct figures if the figure used for the specific heat of ammonia at high temperature was modified slightly. Since this parameter was not known accurately, it was not an unreasonable statement to make.

The disagreement between the two scientists was aired in public at the meeting of the Bunsen Society in the summer of 1907. Nernst gave a paper [16] outlining his experimental results on the position of the ammonia equilibrium and their theoretical treatment according to his Heat Theorem. This was a more detailed version of the note he had sent to Haber the previous year. If Nernst's paper was not well accepted, his Heat Theorem might lose credibility. Haber attended the meeting armed with his experimental data, realising that his reputation was at stake. At the end of Nernst's presentation there was a lively exchange between the two scientists, Haber asserting that Nernst could not be sure he had arrived at the equilibrium position in the absence of decomposition studies, and Nernst claiming that Haber should carry out his experiments at higher pressure where the amounts of ammonia attainable were more amenable to precise measurement. The views of Nernst prevailed, and Haber took this as a personal affront. On returning to Karlsruhe he immediately set up further work on the ammonia equilibrium, this time using a pressure of 30 bar, again in collaboration with Le Rossignol. Haber was fortunate also to have an extremely able mechanic called Kirchenbauer who did the bulk of the construction work on the apparatus.

4. *Work of Haber and Le Rossignol at Elevated Pressure* [18]

The results of the high pressure work were published in 1908. The essential conclusion was that the results obtained at high pressure fully confirmed those obtained by the same authors at normal pressure, and that Nernst's criticism was not valid. Thus Nernst's figures were still lower than those of Haber. In addition, Nernst's data fell more quickly with ascending temperature than did those of Haber. At 1273 K Haber's figures were half as much again as those of Nernst, at 973 K only a quarter as great. Haber ascribed these differences to a number of possible causes: the position of equilibrium was not reached by Nernst, his method of measurement of temperature was subject to inaccuracy and there was a possibility of absorbing ammonia in parts of his apparatus.

In conclusion to this work, Haber stated that the determination of the equilibrium at high pressure and at 973, 1074 and 1174 K yielded results which confirmed the results obtained at atmospheric pressure, and which still departed considerably from the reports of Nernst on the subject. Later, when more reliable figures became available for the specific heat of ammonia at elevated temperatures, Nernst's calculations were seen to correspond with Haber's experimental results.

Thus, at the end of 1907, work by Haber and Nernst had achieved great significance, and had shown why the earlier experimenters had not succeeded in their attempts to make ammonia from the elements. Because of the thermodynamic limitations of equilibrium, at normal pressures only small amounts of ammonia were possible, except at temperatures of 570 K and under, where known catalysts failed to work. Even at elevated pressures, only small amounts of ammonia could be obtained at the temperatures at which catalysts were known to work ($>$810 K). It was clear, therefore, that the transition to the most feasible high pressure would be advantageous, if the idea of a technical exploitation of the reaction was to become at all practical.

D. Attempts at a Technical Exploitation of Ammonia Synthesis [19]

Three years previously, Haber had considered a technical exploitation of ammonia synthesis as impossible, since in the absence of catalysts which would work at low temperatures, the reaction would have to be carried out at elevated pressures and red heat. After having undertaken the higher pressure work with Le Rossignol, Haber's views on the subject changed. He now was of the opinion that, even though only a small part of the hydrogen/nitrogen mixture could be converted to ammonia, a technical process might still be feasible, provided

a) even higher pressures than those so far employed could be used,
b) the high pressure gas was circulated over the catalyst, and
c) the ammonia so synthesised was separated out at high pressure before returning the gas to the catalyst.

In this way, the total quantity of ammonia that could be produced per unit time, (later called the 'space-time-yield'), could be technically profitable, particularly if new catalytic materials could be discovered which were significantly more active than those so far known. Haber's work was now directed towards the development of these ideas. At the same time, his association with the Margulies Brothers ceased. Instead, on the advice of Professor Karl Engler in Karlsruhe, who was an adviser to the board of BASF, he approached the firm for support for his work on the synthesis of ammonia from the elements.

On 15 February 1908, Haber visited BASF in Ludwigshafen. The firm had already supported his studies on the oxidation of nitrogen, and Haber hoped for further financial assistance with his work on the catalytic synthesis of ammonia. The head of the patents department, Professor August Bernthsen, expressed some doubts as to the feasibility of Haber's ideas, but the general director, Heinrich von Brunck, was enthusiastic and an agreement was drawn up between Haber and BASF. Haber made the results of his work available to the works management of BASF, and the personnel in the Nitrogen Section were entrusted with their further development at Ludwigshafen. It must be remembered that it required the strongest belief by Haber that his ideas would come to fruition, since at that time only quite inefficient catalysts were known.

It is interesting to note that Professor Nernst had also approached industry with the idea of exploiting his high pressure equilibrium studies further with a view to a technical synthesis. The director of the chemical firm Griesheim-Elektron, Dr. Bernhard Lepsius, who was an acknowledged specialist in inorganic chemistry, informed Nernst that the practical difficulties involved in working at high pressures and temperatures were too great. Nernst abandoned any hope of finding a technical use for his results.

Haber set about the quest for more efficient catalysts. Iron had been the original catalyst used, and later it was found that manganese was slightly more active than iron, and cerium more active still, allowing the use of lower temperatures. Meanwhile, on the assumption that a better catalyst would be found, he developed the idea of the circulation of the high pressure gas mixture, and the removal from it of the synthesised ammonia without flash evaporation of the high pressure gases. In addition, in order to minimise not only the work of compression, but also the heat requirement, he proposed that the hot exit gas from the catalyst chamber should be used to heat the incoming cold gas mixture; he was familiar with this technique from the commercial apparatus developed by the firm Linde for the liquefaction of gases. The scheme was completed by continually replacing the gas used up to form ammonia by fresh, unreacted gas. The plan was the basis of a patent application by BASF [20], dated October 12th 1908, in which was claimed "a process for the synthetic manufacture of ammonia from the elements, whereby an appropriate mixture of nitrogen and hydrogen was subjected continually to the synthesis of ammonia by means of heated catalysts, and afterwards the ammonia was removed by cooling or absorption, under high pressure, and the heat of the ammonia-containing gas was transferred to the ammonia-free gas mix". A schematic diagram of the set up is shown in Figure 1. At this time, the ideas expressed in the patent were purely theoretical, and BASF were not convinced of the practical feasibility of the proposed process, as it was believed that no steel vessel could contain a continual pressure of 100–200 atmospheres at red heat.

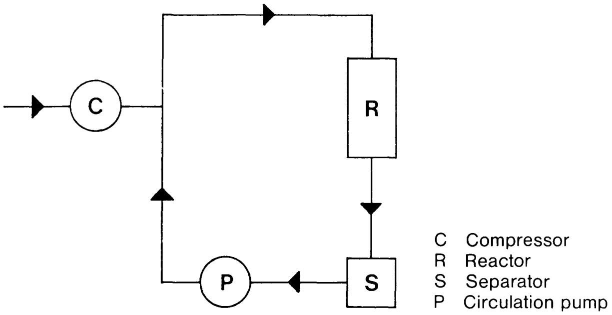


Figure 1. Circulation scheme for ammonia synthesis proposed by Haber

Undaunted by the doubters, Haber and his students worked on, seeking a method of reducing the temperature required to 670–770 K. The problem to be overcome was that, as one reduced the temperature, the rate of reaction became too small. Nevertheless, after a short time, an investigation of the 'higher homologues' of the known catalysts in groups six, seven and eight of the periodic table gave the hoped-for breakthrough.

In March 1909 it was discovered that the precious metal osmium was a surprisingly good catalyst. Haber had obtained some rare metals (e.g. Pt, Os, W, U) from the German Gaslight Society for whom he was a consultant. The sample of osmium was a powder, which was used for osmium lamps, and which was prepared in a secret process which yielded a very fine, amorphous product; this sample was much more active than an earlier sample of osmium prepared by reduction with hydrogen at high temperature. Using this new catalyst, high reaction rates could be obtained at temperatures around 820 K, and so at 175 atmospheres pressure, exit concentrations of ammonia as high as 8% could be obtained. Haber wrote to BASF immediately, informing them of his discovery, but was not pleased with the answer he received. BASF were still sceptical, doubting the practicalities of working at high pressures and temperatures of about 870 K. Engler intervened on Haber's behalf, writing a personal letter to von Brunck, and this resulted in a visit to Karlsruhe by von Brunck and two colleagues, during which heated argument ensued concerning the feasibility of working at high pressure. Von Brunck informed Haber that, on his return to Ludwigshafen, he would seek the advice of the chemist Carl Bosch on the issue, as Bosch had had experience of the iron and steel industry. Bosch's answer was "I believe it can work. I know the capability of the steel industry well enough. It should be risked!". Von Brunck laid much weight on this view. Haber's work was supported energetically, and Haber and Le Rossignol concentrated on the development of a small laboratory apparatus in which it would be possible to circulate gases at high pressure.

Thus, at this point in early 1909, Haber had succeeded in interesting one of the largest chemical companies in Germany in his ideas, and was about to discover whether or not these ideas might be exploited on a practical basis. The BASF chemist Bosch had obviously had a large influence on the decision to continue supporting Haber, and was destined to play an even greater role in the further development of the synthesis of ammonia. He was then 35 years old, six years younger than Haber, and had worked for BASF for almost ten years, gaining a reputation for both thoroughness and innovation. Since he was to become an important figure in the events of the next few years, an investigation of his background, achievements and capabilities is warranted.

3. Bosch's Work on the Fixation of Nitrogen

A. Education of Bosch [21]

Carl Bosch was born on August 27th 1874, in Cologne. His family owned a wholesale business dealing in piping materials for the supply of gas and water, and his uncle, Robert Bosch, was to become the founder of the famous Bosch magneto factory in Stuttgart. As a child, Carl showed a keen interest in natural history, and later, as a teenager, he began carrying out chemical experiments at home. At school he showed promise in the sciences, and

Plate 2. Carl Bosch. (Reproduced with permission from "Im Banne der Chemie, Carl Bosch, Leben und Werk", K. Holdermann, (1953), Econ-Verlag, facing p 16)

decided that he wanted to become a chemist but, before taking up his studies seriously, he spent a year at an iron and steel works, the Marien Works at Kotzenan, where he became familiar with mechanical apparatus. This was on the advice of his father, who considered that knowledge of a more practical application of chemistry would be of benefit to his son. After spending a successful time at the foundry, he began his studies, in 1894, at the Technische Hochschule at Charlottenburg, as a student of foundry technology and machines, but also spent a great deal of time attending lectures in chemistry, from such teachers as Professors Knorr, Rudorf, Liebermann, Witt and Vogel. He learnt much inorganic and organic chemistry and also some analysis, and spent three terms in the inorganic laboratory; all these studies in chemistry were accomplished in addition to his set work on foundry technology. During one of the long vacations, he obtained further practical experience in the Krupp foundry at Neuwied.

Bosch was critical of the teaching of engineering at Charlottenburg, considering it to be far too empirical in nature, and expressed the desire to study pure science (although he later appreciated the engineering experience he had gained.) In the summer of 1896, he began further studies at Leipzig University, working towards a doctorate in the field of organic chemistry under the supervision of Professor Wislencius. Having received his doctorate on 24 May 1898, he became assistant to the professor, a position he held until the following Easter.

At the time Bosch was at Leipzig, German universities were important centres of scientific discovery; many new concepts were being developed within the spheres of chemistry and physics, by such names as Arrhenius and Nernst, and at Leipzig Ostwald was at the forefront of the teaching of the relatively new discipline of physical chemistry. One important aspect of Ostwald's work was the first systematic series of experiments in the field of catalysis. As at Charlottenburg, Bosch again took a particular interest in pure chemistry, but also found time to attend many other lectures on subjects such as mineralogy and microscopy, in addition to his compulsory lectures. He also became known for his extraordinary dexterity in the construction of laboratory apparatus, astonishing his colleagues with a hand-made vacuum pump which he had put together in three days so that he might be able to record the spectrum of helium.

On finishing his studies at Leipzig, Bosch wished to pursue an academic cariier, but his father sought to dissuade him. A visit by Bosch senior to his son in Leipzig resulted in Carl deciding to seek employment in the chemical industry. He made a job application to the Badische Anilin and Soda Fabrik in Ludwigshafen, a company well-known for its notable achievements in the area of dyestuff chemistry and for its willingness to embrace new technology. BASF was at that time enjoying the benefits of a great success, as two years previously the synthesis of the dyestuff indigo had been perfected at Ludwigshafen. In addition, the BASF chemists Rudolf Knietsch was engaged in the technical development of the sulphuric acid contact process, which was destined to become highly-successful. Bosch hoped that a position at such an establishment would offer scope for utilising his scientific education to the full. He took up his appointment as chemist at BASF on April 15th 1899.

B. Early Career of Bosch at BASF [21]

The conditions existing within German industry at that time were very paternalistic, with little freedom, a twelve hour day and few holidays. The normal induction procedure for new chemists, on entering the company, involved a period in the main laboratory, where the individual's aptitudes were explored. Bosch began with the preparation of an intermediate for azo dyestuffs: only a few weeks were necessary to establish his practical proficiency. This preparation marked his first encounter with catalysis. The following year, Knietsch gave him an exercise which was to have a profound meaning in later life.

Professor Ostwald, in Leipzig, believed he had found a catalytic method for the synthesis of ammonia from its elements, a process which, as has already been mentioned, had occupied many chemists for decades. Ostwald had communicated these results to BASF, hoping for financial support to continue his work. BASF showed considerable interest, and gave Bosch the task of verifying Ostwald's findings, which suggested that up to 6% ammonia could be obtained at normal pressure, irrespective of whether ammonia was synthesised from the elements or decomposed into its constituents. After numerous experiments, however, Bosch was obliged to inform the BASF directorate that he could not repeat Ostwald's results. This failure exasperated Ostwald, who admonished the BASF board for setting an inexperienced chemist to the task. Bosch was, however, convinced that he was correct, and defended himself strongly, despite being in a rather difficult situation, his competence as a chemist being challenged by a famous professor of physical chemistry. Bosch had observed that, on using the iron wire in the manner described by Ostwald, an appreciable amount of ammonia was produced, but that this initial rate of production ceased after a short time. After spending some time consulting the literature, familiarising himself with the properties of iron and its compounds, Bosch was able to explain the differences between his and Ostwald's results.

On heating with ammonia, iron forms a nitride which, by treatment at elevated temperature with hydrogen, forms ammonia. Since Ostwald had used the same sample of iron wire for the decomposition and synthesis steps, the source of the discrepancy could be explained. In the decomposition step, iron nitride had been formed which then decomposed, yielding ammonia, in the synthesis step. The fact that Ostwald had also obtained a higher level of ammonia than Bosch in the decomposition step could be explained by the fact that the gases had been passed over the the catalyst too quickly so that the true equilibrium position had not been achieved. Ostwald was greatly disappointed when the true source of the ammonia had been demonstrated, but by this exercise, Bosch had proved himself to be a thorough experimenter.

Over the next few years, Bosch was to gain a reputation as an innovative chemist with both a practical approach and a considerable knowledge of fundamental science; he was often seen at the bench, or in the workshop, carrying out the required practical work himself, which went somewhat against the normal working practices then existing in the great firm. His superiors, Knietsch and von Brunck, realised that the best way to utilise such a strong, singleminded character was to give him as much freedom as possible. Soon, he was given his own laboratory, a workshop, a technician, a chemist and space in an adjacent building in which to carry out larger-scale experiments. He also obtained accommodation in one of the factory houses, an old water tower that had been converted for the purpose of housing young chemists and engineers; he thus settled into working in the chemical industry.

Since first being involved in the problem of nitrogen fixation, via the work of Ostwald, Bosch had been considering ways in which he might attempt to solve it. Von Brunck was convinced it was an important question, and felt that its solution was potentially of greater value to BASF than had been the successful synthesis of indigo, so he initiated a considerable effort on the arc process. Two members of the BASF staff, Schonherr and Hessberger, had developed an electric arc furnace at about the same time as the Norwegians. Bosch soon joined this work, with the task of improving the conversion of the gas from the electric arc to nitrates, and was allocated a dextrous glassblower, Kranz, as an assistant. As has already been noted, the fixation of nitrogen by this route was very expensive, since much of the energy was lost, and, unlike Norway, Germany did not possess cheap water power. Thus, for the process to be viable, the combination of nitrogen with another species had to be effected at a lower temperature, so a method was sought which did not require an electric arc. BASF was apparently well-placed to attempt the solution of this problem. Through their association with the sulphuric acid work, Knietsch and Dr. Eugen Sapper, Bosch's immediate superiors, possessed considerable experience in dealing with catalysts and large quantities of gas, and also with the building of new apparatus. Bosch had already shown himself a capable and thorough experimenter. A start was made on the work in the spring of 1902.

Bosch began by following up all the possible lines of research to be found in the literature, and became interested in the cyanamide process, wherein nitrogen reacted with a glowing mixture of barium carbonate and carbon to yield a mixture of barium cyanide and cyanamide, which was easily converted to ammonia. Bosch considered that this reaction was worth further investigation, and requested a physical chemist to assist him in his work. Professor Bodenstein, in Leipzig, recommended Dr. Alwin Mittasch, a school teacher who, in addition to his school duties, had studied chemistry under Ostwald and Bodenstein, and thus had received an extensive grounding in physical chemistry and catalysis. Mittasch, who stood only five feet tall, joined BASF in March 1904, spent the customary probation period in the main laboratory successfully, and was assigned to the investigation of the interaction of nitrogen with barium carbonate and carbon. Bosch was a demanding supervisor, requiring that everything that could possibly be measured was measured; this was extremely valuable to Mittasch, an inexperienced newcomer to industrial research, and during this period he became familiar with the use of various instruments for measuring flow rates, temperatures and the composition of gases.

The nitrogen used in this reaction had to be extremely pure. Bosch considered various methods for the preparation of pure nitrogen, including the removal of the oxygen from air by means of glowing copper, and the removal, by the use of potash solutions, of carbon dioxide from gas streams after effecting the combustion of various gases in air. In addition to the problems associated with the preparation of pure gases, new apparatus, capable of withstanding extremely high temperatures, had to be devised and constructed. Despite the immense amount of work carried out, the difficulties

Plate 3. Alwin Mittasch. Photo: Deutsches Museum München

remained apparently insurmountable, and by 1907 still no satisfactory method had been devised whereby nitrogen could be 'fixed' at temperatures below 1770 K. Many individual successes had been achieved, and various patents were generated from this work, but the fact remained that the fixation of nitrogen still relied on the use of extremely high temperatures.

In the summer of 1907, a large plant was built for the preparation of barium cyanide. From this plant, 5000 kg of cyanide mass could be produced in a day, and from this, 300–350 kg of ammonia was obtainable, rather than the 400–500 kg predicted from the laboratory-scale experiments. The cost of the plant was unexpectedly high, and many difficulties were encountered due to the failure of ceramic materials, despite extensive investigation of such materials beforehand in the laboratory. After the production of about 90,000 kg of cyanide mass had been effected, at enormous cost, the decision was made to shut the plant down in June of the following year. Bosch had not been working exclusively on this route for nitrogen fixation. He and Mittasch had been investigating other nitriding reactions, using titanium, silicon and aluminium, and were not relying solely upon the success of the barium cyanide venture. Gradually, however, it began to appear that the experiments with the nitrides of various elements had been taken to such a point that the aim of fixing nitrogen without the aid of an electric arc was unattainable. It was at this time that Haber approached BASF with the results of his work on the fixation of nitrogen by means of its reaction with hydrogen over a catalyst. The firm had already sponsored some investigations by Haber on the efficiency of the arc process, but it was the catalytic synthesis of ammonia which was now to prove decisive in BASF's attempts to solve the nitrogen problem.

C. Visit to Karlsruhe [21, 22]

During 1908 and 1909, Haber and Le Rossignol had worked on, developing a small laboratory apparatus in which it was possible to circulate gases at high pressure, and in July 1909, representatives from BASF were invited to inspect it. On July 2nd, Bosch visited Karlsruhe, accompanied by Mittasch and Kranz, the technician, and since some members of the BASF management still did not believe Haber's results, this demonstration was of vital importance to Haber and Le Rossignol. Unfortunately, however, things did not proceed smoothly. The apparatus sprang a leak, and the demonstration had to be interrupted for a few hours whilst repairs were made. Bosch had watched the proceedings so far, calmly and patiently, but now decided he could not

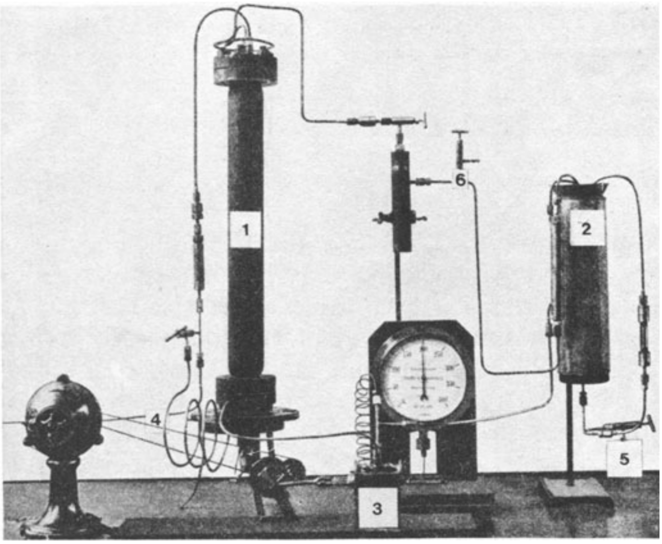


Plate 4. Haber and Le Rossignol's recirculatory system for the preparation of ammonia. (Reproduced with permission from F. Haber, Z. Elek., 16, 244, (1910), Verlag Chemie)
1 Catalytic vessel with heat exchanger, 2 Condenser, 3 High pressure circulation pump, 4 Fresh gas feed, 5 Ammonia outlet, 6 Sample line

wait until the repair had been carried out, as he had pressing business in Ludwigshafen. He outlined to Kranz means whereby repeated failure of the particular seal could be avoided, and deemed it unnecessary to wait to see how the apparatus worked, as he could imagine it well enough. To the great disappointment of Haber and Le Rossignol, he and Kranz returned to BASF. Only Mittasch remained, and he became the first member of the firm to witness the appearance of ammonia in the receiver of the small apparatus.

Haber's small apparatus consisted of an upright furnace of about 750 mm in height, provided with a heat exchanger and an electrically-powered upper preheat section. Beneath the heating coil there was a shelved insert of sieve platelets on which osmium powder was sprinkled, and underneath the catalyst space was the heat exchanger, through which the incoming cold gas was preheated. The temperature at the upper end of the catalytic section was about 1170 K, and at the lower end 870 K. The high pressure furnace formed part of a recycle apparatus in which a circulation pump continually fed compressed gas, and a separation tube, maintained at 233 K, condensed the ammonia. Under a pressure of 185 atmospheres, this apparatus yielded 90 grams of ammonia per hour at a concentration in the effluent gas of 2.8 volume percent, using a charge of catalyst of 98 grams of osmium.

On March 18th 1910, at a meeting of the Scientific Society at Karlsruhe, Haber gave a lecture, illustrated by experiment, to demonstrate the new technique for the fixation of nitrogen. The accompanying photograph of the original recirculatory system (Plate 4) is taken from the account of the lecture given in the literature [23]. The lecture excited great interest, accounts even being given in the popular press, and Haber achieved considerable fame. In 1909, a thorough account [24] of the work carried out by Haber and Le Rossignol on this system was submitted, in manuscript form, to BASF, for their approval to publish. It contained a detailed account of the theoretical and practical aspects of the synthesis and separation of ammonia. Agreement to publish was granted, in principle, after the removal of some comercially-valuable information, but the actual publication of the paper was suppressed until 1913. In the paper, Haber expressed the hope that "the way forward will be opened for a new industry".

D. Further Work Carried Out by Haber

Between 1910 and 1912, Haber and his students carried out further thermodynamic and kinetic studies related to ammonia synthesis. Redeterminations of the precise position of the equilibrium at various temperatures and pressures were carried out, as were measurements of the heat of formation of ammonia as a function of temperature. The activities of several catalysts (uranium, osmium, molybdenum and tungsten) were determined, and efforts were made to identify the factors influencing the rate of reaction; seven papers were later published (1914–15) [25–31] summarising all of this work. The appointment of Haber to the directorship of the Kaiser Wilhelm Institute in Berlin, in 1912, signalled the end of his involvement in work on ammonia synthesis.

It is interesting that Haber made a settlement with BASF which allowed him a flat sum of one pfennig for every kilogram of ammonia that might be sold [2]. He had considered that this arrangement was likely to be more favourable than a simple percentage of sales, as the price of ammonia was likely to fall as production rates increased. Le Rossignol and Kirchenbauer became co-beneficiaries of Haber's arrangement.

E. Initial Progress at Ludwigshafen [21]

1. The Problems Ahead

Only a few weeks after von Brunck's visit to Karlsruhe, Haber had successfully demonstrated that ammonia could be produced from his small experimental apparatus. Von Brunck now put a great deal of effort into developing Haber's ideas further at BASF so that a large-scale manufacturing process at Ludwigshafen might become a reality. Characteristically, he moved rapidly, and on a large scale. Bosch was given extensive powers to progress the project. He was the ideal man for the job, being a chemist with experience of iron and steel technology, and great enthusiasm for the construction of apparatus. He was broad in approach, possessed an extensive fundamental knowledge of science, and in addition he had acquired valuable experience in dealing with large quantities of gas during eight years' acquaintance with the nitrogen problem.

Bosch faced three problems, all of which had to be solved before the construction of a factory could be contemplated. First of all, it was clear that osmium was not suitable as a basis for a technical synthesis, because of its high cost, scarcity and tendency to oxidise to osmium tetroxide. The whole world's supply, obtainable as an impurity in crude platinum, only amounted to about 100 kilograms. Also, Haber's later catalyst, uranium, a discovery made after the successful demonstration of the recirculatory apparatus, was rare and sensitive to moisture. Thus, it was necessary to seek new catalysts which were cheaper and easier to handle.

The second problem facing Bosch concerned the construction of apparatus. The technology of the time could furnish no examples of vessels which were required to contain high pressure gases at high temperature. Most chemical reactions of technical importance occurred at normal pressures, and the one example of a process operating at high pressure, the Linde process for the liquefaction of the air, required the containment of 200 atmospheres at a maximum temperature not exceeding that of ambient air. The copper apparatus used here, with its soft soldering, was not suitable for temperatures up to 870 K, so the design and construction of apparatus was obviously an exercise of vital importance to the success of the enterprise.

Thirdly, it was necessary to supply the raw materials, nitrogen and hydrogen, in sufficient quantity and purity for the full-scale unit. The contemporary processes for the production of hydrogen were all to prove too expensive and to yield gas too impure for use in the catalytic reaction, so the provision of a suitable process for hydrogen production was also of great importance.

Work aimed at the solution of all three problems was set underway simultaneously in the summer of 1909, and as the enormity of the project became apparent, many experts considered that Bosch had undertaken a task that was impossible to achieve. Even among his colleagues, scepticism was rife, opinions being expressed that the enterprise would eventually be the ruination of the firm. Bosch was not concerned by these views, and immediately set about the task of setting up a workshop and the gathering together of a team of coworkers suitable for the work ahead. He required workers who could work precisely and reliably, and who were capable of tackling new and unusual concepts quickly and without prejudice, but as he sought them out he met resistance. The normal working practices of the firm were well-structured, with separate departments being responsible for individual areas of work, but Bosch preferred to supervise all work personally, testing out and proving all processes himself. This alienated some of the established engineers, who declined to join him in the venture, so he was obliged to recruit younger engineers, and Franz Lappe, who had studied with Professor Bach at Stuttgart, specialising in metal work, joined the project. Lappe typified the commitment and optimism which Bosch was seeking.

Bosch put great reliance on independent thought, reliability and positive attitude. He considered a fundamental chemical education to be the prerequisite for success in all areas to be investigated, setting less value on specialism, which he believed to lead to a narrow approach to problem solving. Chemists were assigned preferentially to engineering exercises. His own experiences at Charlottenburg had led him to develop a distrust of the education of engineers, which he believed provided them with insufficient chemical grounding. However, an engineer who had a fundamental command of physics or thermodynamics was just as welcome to the team as a chemist.

By these criteria, Bosch surrounded himself with capable coworkers, and embarked on the daunting tasks with a small, inexpensive workshop consisting of one large and one small lathe, a drilling machine, a turner, a fitter and an assistant. Showing a characteristic distaste for beauracracy, he combed the entire factory for ideas which might be useful in the work. Again, this was unusual at BASF, which was not organised to accomodate such independence, but Bosch had the backing of the directorate, which had, by then, allocated a million marks for the ammonia synthesis work, and awaited a positive result to justify such expense. Bosch made Mittasch responsible for the catalytic work, and took charge of the problems related to the high pressure apparatus and hydrogen supply himself. The two men were opposite in character and approach. Bosch saw things on a large scale, was impulsive and generated a continual stream of ideas. He worked rapidly, and made few notes, preferring to rely mainly on his memory. He was quick to assess the possible practical application of an idea, and made decisions equally speedily. In contrast, Mittasch favoured the systematic, logical approach, making reasoned deductions from careful observations, and keeping extensive, accurate notes. Despite these differences in approach, both men shared a total commitment to precise experimental work. Like Haber, Bosch frequently worked late into the night, and had no time for those who did not share his dedication to the tasks in hand.

a) The Search for the catalyst [21, 22, 32]

The first exercise was to repeat Haber's results. The board had already taken the precaution of obtaining options on the world's supply of osmium, and it was now necessary to obtain pressure vessels and ancillary equipment for the construction of catalyst testing equipment. A skilled fitter was despatched to Karlsruhe to become familiar with the construction of Haber's apparatus, and in the summer of 1909 a high pressure rig, based upon Haber's heated catalytic vessel, was made ready in the phthalic acid laboratory. Initially there were two or three catalytic vessels capable of taking a few grams of catalyst, and a unit was constructed to provide the hydrogen/nitrogen mixture. A combustion furnace took in hydrogen/air mixtures, and produced nitrogen, containing hydrogen, to which was added some electrolytic hydrogen in order to achieve stoichiometric proportions. A heated palladium/asbestos tube was used to remove the last traces of oxygen from the gas mixture. A compressor was supplied, which allowed pressures of up to 200 atmospheres to be obtained, and the compressed gas was stored in a high pressure battery, from which it could be distributed to test units within the building, via a high pressure manifold.

The first attempts failed to achieve the ammonia concentrations obtained by Haber; erratic results were obtained, and a large amount of osmium was lost as volatile osmium tetroxide. More osmium was obtained from the options taken up, and, finally, Haber's results were replicated. Mittasch had divided the work into two areas; attempts at improving the activity of iron were to be carried out in conjunction with Dr. Hans Wolf, while, with Dr. Georg Stern, he would investigate all other elements. What was the reason for the belief of Mittasch and Bosch that success could be achieved with iron? Nernst and Haber had used iron in their studies, but had not achieved results that gave good reason for optimism. Iron did possess obvious fundamental advantages over osmium and uranium, being cheap and abundant, and it was known that iron easily effected the decomposition of ammonia to hydrogen and nitrogen, at red heat. It was, therefore, considered not unreasonable to expect it to be able to catalyse the formation of ammonia, and so it seemed a profitable line of research to follow. Mittasch, in his earlier work at BASF on nitrogen fixation, had investigated the optimal conditions for the formation of many nitrides, and also ammonia. From this work arose the idea of multicomponent catalysts. If it was assumed that a labile iron nitride was an intermediate in the catalytic synthesis of ammonia, then any addition to the iron which favoured the formation of such a nitride might be advantageous: such additives were termed 'flux promoters'. So Mittasch and his coworkers began to test the activity of all available types of iron and iron compounds and ores, experiments being carried out on the materials as supplied, as well as after the addition of various other compounds. In particular, various catalysts were made on the 'flux promoter' principle, chlorides, sulphates and fluorides of the alkali metals and alkaline earths being added to the iron compounds.

The initial results of these experiments were disappointing, and the degree of success did not seem commensurate with the efforts expended. Despite many variations in the preparative conditions of the iron, and on the nature of the additives, often no ammonia was obtained, and in other cases only small amounts were observed; no degree of uniformity was observed in the results. Bosch was, at that time, aware of a patent from Schering concerning the effect of alkali on the activity of nickel catalysts for the catalytic dehydrogenation of borneol to camphor, and he believed that this might shed some light on the various effects occurring with the iron catalysts, but the results obtained thus far showed that alkalies had only a very small effect on the activity of iron.

During the course of these experiments, a particular form of iron oxide, 'crocus martis', obtained from Merck, yielded a favourable result, but again this was found to be very variable. Haber's apparatus was proving too complicated to enable sufficient rapidity to be achieved in the testing of samples, as it was necessary to dismantle the apparatus completely every time a catalyst change was carried out. Stern devised a much simpler arrangement, consisting of a steel tube of about half a meter in length with internal electric heating and air cooling. It had a small, removable catalyst container which could take about two grams of materials, and which was easily accessible by the turning of handles; two dozen of these vessels were constructed, enabling the rapid evaluation of many hundreds of catalysts. On November 6th, a much more favourable result was obtained with a sample of Swedish magnetite from Gallivare, which had stood on the laboratory shelf for many years. Under the experimental conditions, 3 % by volume of ammonia was achieved in the exit gas, compared with less than 1 % in the best of the previous experiments. The activity of this material was not improved by the addition of alkali nor alkaline earths. The particular efficacy of this iron compound was ascribed, initially, to its physical state rather than to the additives it contained; it was particularly dense, but also granular and crumbly, and offered much more finely-divided metal area than had the other catalysts previously tried. Thus, the 'compact-porous' nature was considered important, and a patent [33] was submitted in November 1909, claiming the discovery of "catalytic materials for the synthesis of ammonia from its elements, in that the catalytic material has a compact yet porous form". The catalysts appeared to be more effective the higher the specific weight, which seemed to contradict the expected effect of metals on supports; iron catalysts consisting of finely-divided powders, and as thin coatings on inert supports, were far less active than the denser forms.

It soon became apparent that it was impossible for this extreme view of a compact, porous mass to persist, as it was discovered that numerous other compact-porous forms of iron, including other magnetite samples, were not as active. It was concluded that, while structural factors might well be important, the composition of the material must be the predominant factor influencing its activity. Despite the variability of the results, by the beginning of 1910 there had been a sufficient number of clear examples of specific promoting effects to enable a patent application [34] to be made relating to the use of promoted catalytic material for the synthesis of ammonia.

The catalytic work had taken a decisive turn, and, by January 1910, Mittasch and his team had discovered an iron catalyst, containing small amounts of impurities, which was capable of producing as much ammonia as previously obtainable with osmium and uranium. On hearing of the success with the iron catalysts, Haber sent the following letter to the BASF board, on January 17th 1910 [21, 22].

> "*It makes me extraordinarily happy that Herr Bosch and his coworkers have made this great step forward in the area of ammonia synthesis. I congratulate you. It is remarkable how matter continually reveals new facets. Iron, with which Oswald first worked, and which we have studied a hundred times in the pure state, now works in the impure state. I recognise that every trail must be followed to the end. Again, I congratulate Bosch, and hope to learn more news from him tomorrow.*"

Haber was very interested to see how the success had been achieved, and arranged to visit Ludwigshafen. The news that the professor was to visit caused much excitement amongst the team; he was conducted around the workshop in which the catalytic vessels were made, visited the laboratory, and also saw progress being made on the construction of larger-scale, high pressure facilities. These experiments were to be conducted in a reinforced, explosion-proof concrete bunker situated at the extreme northernmost tip of the works.

The original patent application relating to promoted catalysts marked the beginning of an extensive programme of systematic experiments. Attempts were made to reproduce the activity of the highly-active magnetite sample, but, although many synthetic magnetites were prepared, none was as active as the Swedish variety. It was clear, from the literature of the time, that natural magnetites could contain various impurities. Experiments were carried out to mimic the exact chemical composition of the Gallivare magnetite, by preparing melts consisting of iron oxide and various other oxides, and good results were obtained. It was obvious, therefore, that the chemical composition of the magnetite was very important to its catalytic activity, so the experimental programme shifted from the synthesis of magnetites of definite composition, to the systematic study of the influence of all possible additives on iron. To this end, it was necessary that the following conditions be fulfilled. Firstly, the catalyst samples should be prepared from iron of the highest purity obtainable, and two such varieties of iron were obtained from Kahlbaums in Berlin, the purer form being twice as expensive as silver. Secondly, special methods had to be developed for the preparation of intimate mixtures of catalyst and additive; fusion of the metallic iron and additive under pure oxygen was used initially, and later other methods were employed. Finally, the synthesis gas used in the experiments had to be of the highest-possible purity, and, to this end, electrolytically-produced hydrogen and oxygen-free nitrogen were supplied.

Many samples of iron catalysts, containing a single additive, were prepared and investigated for activity. The initial results of these investigations revealed that iron alone was only slightly catalytically active, but could be improved (promoted) or worsened (poisoned) by specific additives. By March 21st

1910, it had been realised that it was probably more important to exclude harmful additives than to include favourable ones. Further systematic experiments were carried out on the promotion and poisoning of iron (and also cobalt and nickel) using the test units simultaneously, arranged in a battery; in this way, fifty to a hundred materials could be tested per week. Up until May 1910, the catalytic samples had all been produced using the melt method. Experiments were then conducted in which additives were incorporated into the iron by wet methods, e.g. by coprecipitation of mixed metal nitrates with pure ammonia, followed by evaporation and heating to dryness in a quartz tube, or by solution of the iron and additive in nitric acid with subsequent evaporation and calcination. This nitrate method was capable of various modifications; iron powder could be impregnated directly with the additive in the form of a nitrate solution, and then calcined, or water-insoluble oxide could be stirred into molten iron nitrate. The various preparative methods gave essentially the same results in terms of catalytic activity, although some differences did exist which were attributed to a more or less perfect distribution of the additive in the iron. The wet methods allowed the production of certain catalytic materials which were not possible by the fusion method.

These systematic experiments led to the following broad conclusions.

i The catalytic activity of iron is improved by the incorporation of finely-divided metal oxides, particularly those oxides which, by virtue of their high melting points and resistance to reduction, present an unchanged structure in the iron. Examples of such promoters are alumina and magnesia, and, to a lesser extent, calcium oxide and barium oxide. Only very small amounts are usually required for the effect to become apparent.

ii The activity of iron is adversely affected by certain substances, particularly sulphur, phosphorus, arsenic and chlorine. Levels of as low as 0.01 % can be harmful, and if these rise to 0.1 %, can completely inhibit the catalytic activity. This was a particularly important discovery, as it explained why so many failures had been observed with iron compounds in the past, since most of the iron preparations used contained sulphur as a result of their method of manufacture.

iii The addition of certain metals and oxides to iron catalysts proved to be of no effect, e.g. copper, silver and titanium dioxide.

iv In the case of the simultaneous presence of promotors and poisons, a limited compensation effect might be observed, but the overall activity is always less than in the absence of the poison.

v Further improvements can be achieved by producing catalysts from mixtures of more than two components. For example, the combination of iron and alumina can be favourably influenced by small amounts of potash.

vi Enhanced activity is observed for combinations of iron with other catalytically-active metals such as cobalt, molybdenum, tungsten and uranium. This effect was termed ‘mutual activation’.

vii Metals which catalyse the ammonia synthesis reaction (osmium, ruthenium, uranium, molybdenum) can also be promoted by added substances, but do not all show improvements of the same magnitude as iron. The type and amount of promoter has to be varied from one metal to another. Typical examples of such combinations are osmium-potassium oxide and nickel-molybdenum.

viii A support effect, such as observed in the classical case of platinised asbestos, is of negligible importance with ammonia catalysts, (except with osmium and ruthenium).

ix It is necessary to use as pure source of iron as possible in order to avoid poisons. High temperatures are useful in removing volatile poisons, but a single heat treatment is not usually sufficient.

x It is particularly important that all the gases used are pure and kept in a pure state. Sulphur-free hydrogen should be employed, and all oxygen compounds should be removed from the gas stream.

These results were published in a series of patents [35].

Further discoveries were then made concerning the effect of sintering. The use of similar materials of the same chemical composition, treated under the same reduction conditions, could produce catalysts of differing catalytic activities, depending on whether the preparation involved high or low temperatures. Low reduction temperatures were found to be advantageous, and it was inadvisable to go beyond temperatures which corresponded to the operating conditions. The extent of sintering was found to vary from metal to metal, but could be significantly different depending on the purity of the metal.

After the initial discovery of the active iron catalyst, further work was carried out to determine whether better catalysts could be found, and to develop a formulation which would be utilisable in the large-scale operations planned at BASF. Ultimately, it was envisiged that the catalyst would also be sold externally. Mittasch and his coworkers tested over 20,000 catalysts, and, in an elegant and throrough fashion, produced a comprehensive picture of the relative activities of various metals for the synthesis of ammonia, and also of the specific effects of promoters on these metals. The promoter studies were particularly interesting. Mittasch discovered that no sharp demarcation existed between the promoting and indifferent components, nor between the indifferent and the harmful ones. The important factors were the proportions of additive used and the structures of the solid products obtained; comparison of the effects of additives on various catalysts revealed the high specificity of promoter action. A particular promoter did not necessarily act in the same sense and to the same extent on different metals.

During the course of these systematic investigations, it became obvious that the iron-alumina-potash combination was the most suitable catalyst for use in the large-scale synthesis of ammonia; despite extensive work, and the gathering together of a great deal of fundamental knowledge, the promoted iron catalyst was not surpassed by any other catalyst.

b) Development of the high pressure apparatus [21, 36]

At the same time that the catalytic studies were showing the first signs of success, an experimental unit was being constructed which, it was hoped, would enable scale up of the laboratory experiments by a factor of a thousand. The small-scale catalytic reactors operated with a few grams of catalyst whereas the vessel proposed for the larger scale work would contain a few kilograms. At the beginning of 1910, construction started on a vessel consisting of a steel tube of about 1 meter in length, 70 mm in diameter, and wall thickness of 30 mm, which was to be connected to a circulation pump and an ammonia separator. It was essentially the same set-up as that used by Haber, but somewhat larger; it was completed in early spring.

The vessel was heated electrically, using external nickel windings, and it had an internal heat exchanger. A small circulation pump enabled a flow rate of 50 litres per hour of compressed gas to be achieved. A chiller unit, containing a toluene-carbon dioxide mixture, was provided for the separation of the ammonia. A battery of compressed hydrogen/nitrogen gas mixture provided the fresh gas. Two catalytic vessels of the new design were enclosed in an explosion-proof concrete bunker, which lay a considerable distance from all other work, and was shielded by walls of black iron plate, since Bosch had already learnt of the dangers of fire and jets of flame caused by self-ignition of escaping jets of high pressure hydrogen. Inlet and exit connections and all services were led through the concrete walls to the rest of the plant. The planned experimental conditions were 100 atmospheres and 870 K, and the first catalyst used in this large scale apparatus was the Swedish magnetite, which had performed so well in the recent laboratory investigations.

Experiments with this larger vessel came to a rapid end, however; it operated for only 80 hours, then burst. Had the catalyst been osmium, instead of the newly-discovered iron catalyst, the whole world's supply of the precious metal would have been lost! The performance of the steel tubes used as catalytic vessels had been much worse than would have been expected had they contained air at the same temperature and pressure. Investigation of the failed tube showed that it had swollen, and that the inner wall had completely lost its tensile strength, apparently by some change in the material of its construction. The alteration was stepwise, until finally the undamaged part had become so thin that the internal pressure had caused it to rupture. The immediate conclusion was that it had suffered chemical attack. At first, hydrogen was considered harmless, but nitrogen was suspected, as it was known from the literature that iron and ammonia could form iron nitride, a silvery-lustrous, brittle compound; however, chemical investigation revealed no trace of nitrogen in the brittle material.

Bosch investigated the failure of the steel personally, in a thorough fashion. He prepared ground sections, and examined them by means of a metallographic etching process, a technique then almost unknown in the chemical industry, but known to him because of his earlier experience in the iron and steel industry. This investigation revealed a zone of light colouration at the surface of the steel which had come into contact with the high pressure gases.

Carbon-containing steel had been chosen for the material of construction of the pressure vessel because of it mechanical strength; it is usually dark in colour because of the carbon-containing perlite interspersed in a matrix of pure iron. Bosch observed that the perlite had disappeared from the lightened inner portion of the tube, and the structure of the steel had been broken down by fissuring. Decarbonisation of the steel had also occurred, but it was obvious that no pure, soft iron had been formed because the altered material was hard and brittle; it appeared that hydrogen had combined with the iron to give a brittle alloy. In addition to this embrittlement, the steel had been weakened further as a result of the formation, during the decarbonisation process, of methane occluded under high pressure within the steel: in association with mechanical strain, this contributed to the disintegration of the structure. In the case of rapid depressurisation of the surrounding gas atmosphere, the occluded gas could form bubble-shaped bulges in the material, particularly if this occurred at high temperature.

Thus it had been determined that the diminution of the mechanical resistance of steel, by the action of hydrogen under high pressure and temperature, was due to two processes, i.e. decarbonisation, and dissolution of hydrogen in iron. A series of experiments was performed, with the aim of overcoming this newly-encountered difficulty. Although the first synthetic ammonia was made in the experimental unit on May 18th, no real sense of success was felt, since the vessels always failed after a short time on line. During these first months, most of the time was taken up with repairs, a run lasting between one and two days being the best that could be hoped for. In order to maintain the temperature inside the oven at 870 K, local overheating of the vessel walls (up to 1070 K) was unavoidable, since external heating was being used. Also, despite the fact that the synthesis of ammonia from its elements was an exothermic reaction, and it should have been possible to maintain the temperature of the vessel, once the reaction was underway, without additional input of heat, autothermal operation was not possible in these early stages. There was a conflict of requirements. The length of time to failure of the vessel was increased, by means of careful avoidance of overheating, but, as laboratory experiments confirmed, carbon steel at high pressure and temperature was always transformed by hydrogen in this manner. It was merely a question of how long it took. Repeated experiments showed that, even using the best-available catalysts which permitted operation of around 670–720 K, the vessels lasted only a matter of days.

Various measures were considered as means to overcome the problem. Replacement of the external method of heating by internal heating, together with the use of a strong internal insulation and external cooling was proposed, but at first proved to be unsuitable and uneconomic. The insulation material, under high pressure conditions in the presence of hydrogen, had a tendency to break down, and even that which remained intact had a high heat conductance in the presence of high pressure hydrogen. It appeared, at that time, that the idea of using steel as the material of construction of the pressure vessel would have to be abandoned, and a further series of systematic experiments was conducted to investigate all possible metals and materials which could be used as alternatives for the construction of the vessel. However, no other metal was comparable with steel in strength and ability to contain high pressures of hundreds of atmospheres, and the samples tested either disintegrated or allowed hydrogen to diffuse through very easily. The position appeared hopeless, and even Bosch himself began to believe that a solution to the problem of the pressure vessel would not be found.

Meanwhile, an idea developed for a general solution to the production of such an apparatus. It was accepted that the decarbonisation of perlite and the concomitant formation of brittle iron hydride was unavoidable, so means were sought by which this alteration in structure could be accommodated and rendered harmless. The functions of the wall of the vessel were twofold: it took the pressure of the highly-compressed gases, and it provided a gas-tight seal. Bosch attempted to separate the two functions of the vessel wall, utilising two different materials of construction for the two separate duties. The first such vessel consisted of a steel tube lined on the inside by a tube of fine silver of 2–3 mm wall thickness. Unfortunately, owing to the differing rates of thermal expansion of the two materials, the silver tube buckled on heating, and on cooling an end was torn off. There had been great hopes for the lined tube, and the failure was a severe setback for Bosch and his team. The failed apparatus was examined thoroughly by Bosch, who carried out a microscopical investigation of samples removed from the vessel. One Saturday morning at the beginning of February 1911, work was progressing on the problem, with alternatives such as the use of a bronze inner lining being discussed as a last resort, when Bosch suddenly arrived at the solution. He announced, in dramatic fashion, "Use soft iron!". Since soft iron contains only a very small amount of carbon it cannot be damaged by decarbonisation. Although the soft iron would suffer chemical change by reaction with hydrogen, a brittle hydride being produced, once this had occurred the inner lining could suffer no further alteration, and, although embrittled, would still retain its ability to contain the gases, provided it was enclosed in a pressure-resistant shell.

Soon after this concept arose, Bosch had another idea which contributed the final piece of technology leading to the solution of the problem of the apparatus; apparently this idea came to him on the way to his office one morning. He proposed that the outer steel tube should be bored with small holes, without affecting its mechanical strength. The hydrogen, which diffused through the inner soft iron lining, could then escape before having the opportunity to build up any significant pressure. In this way, the outer vessel could be protected from hydrogen attack, and should, therefore, maintain its mechanical integrity. This idea arose by inspiration, and Bosch immediately asked the patents department to lodge an application. It was this advance which allowed the technical exploitation of Haber's process to become a reality.

A new vessel was constructed, in accordance with the new criteria, consisting of a perforated steel outer shell with a soft iron lining; once the soft lining had become brittle due to formation of hydride, it could suffer no further distortion or failure, because it lay snugly against the outer tube.

The inner tube contained the gas (except for a small amount of hydrogen which diffused through the wall), and the outer tube withstood the high pressure; in practice, losses of hydrogen through the perforated outer wall were minimal. The inner tube bore the chemical attack and protected the outer pressure vessel from corrosion.

The whole development of the technical process depended, more or less, on the solution to this problem. The first such double tube was put into operation on 5th March 1911; it continued beyond normal expectations, and after it had been on line until the end of April 1911, von Brunck was ready to put the whole of the financial might of BASF behind the development of the large scale synthesis of ammonia. Von Brunck had already had the experience of staking large sums of money on one project — the synthesis of indigo. The participation in the Norwegian saltpeter undertaking was dissolved, the majority of BASF's interest in it being sold, and various other projects were also given up at that time, in order to concentrate on the synthesis of ammonia.

c) The supply of pure gases [21, 22]

The third major problem which Bosch and his team had been addressing was the production of the reactant gases in sufficient quantity and of sufficient purity. The catalytic experiments had demonstrated the importance of the use of gases of the highest purity, and the cost of the hydrogen now became of vital importance to the profitability of a large-scale operation.

Since the summer of 1910, after the initial success of the catalytic studies, the facilities of the redundant barium cyanide plant had been allocated to the ammonia synthesis project. Work began on the construction of a pilot plant, which was to be used to investigate all aspects of the process. Supplies of hydrogen and nitrogen were already available on the barium cyanide plant; the source of hydrogen was the nearby chlorine works, where pure hydrogen was generated electrolytically, and a process for the production of nitrogen had been developed, in which electrolytic hydrogen was burnt in air.

The pilot plant was soon established, and by the beginning of 1911 it could be regarded as a small-scale manufacturing plant, being capable of producing about 25 kg of ammonia a day. By this time the original idea of using refrigeration to effect the separation of ammonia had been replaced by the injection of water to form an ammoniacal solution. Further improvements were made to the catalytic pressure vessel; gas heating was substituted for the electric heating coils, and was found to be easier to control, although continual input of heat was still required to maintain the reactor temperatures. A large step forward was made when, in mid 1911, by improvements in the insulation and heat recovery, a vessel containing 5 kg of catalyst was maintained for the first time at high temperature by its own heat of reaction. As improvements were made, the production capacity of the pilot plant rose steadily, reaching 100 kg a day in July 1911.

The main source of hydrogen used thus far had been electrolytic hydrogen, which, although eminently suitable for experimental work because of its high purity, was obviously not a viable proposition for use on a large scale, on account of its very high cost. So Bosch and his coworkers had been investigating alternative methods for the production of hydrogen. A cheap, readily-available source of hydrogen could be obtained using the well-known water gas process, in which steam was blown over white hot coke to give a mixture of equal volumes of hydrogen and carbon monoxide. In order to obtain pure hydrogen, it was necessary successfully to remove not only the carbon monoxide, but also the sulphur-containing compounds, with which water gas was always contaminated. The Linde refrigeration process, used to obtain nitrogen from the air, appeared to be a suitable method for removing, by liquefaction, most of the impurities from the water gas, and further work was carried out to investigate the utility of the process.

An alternative process for generating purer hydrogen was considered, in which steam was decomposed over red hot iron; at first it appeared promising, but it was later rejected as the regeneration of the oxidised iron mass was found to require too much reduction gas, and the iron gradually sintered becoming less efficient in effecting the reaction.

Thus, the production of the two reactant gases, in sufficient purity, for use on the large-scale plant, was to be by refrigeration; nitrogen would be obtained from the air, and hydrogen would be won from water gas. Refrigeration did not, however, remove all traces of carbon monoxide and sulphur compounds from the gas stream, so a further purification step was necessary; Bosch hoped to use a method which had been employed in the manufacture of formic acid salts, namely the absorption of impurities in hot caustic soda solution under pressure.

F. Decision to Go Full-Scale: Further Problems to be Overcome [21]

Meanwhile, in the summer of 1911, the board of BASF was making important decisions concerning the future of the ammonia synthesis project. In September of that year, land was acquired in the neighbourhood of Oppau, on the northern edge of the Ludwigshafen works; drawings were begun for a large ammonia factory, and the plans were ready in only a few weeks. The building plans were submitted in November. Although the decision to build the factory had been made, many difficulties still remained to be overcome. The technology was completely new, and still carried with it considerable risks. It was obvious that, since the project relied on the proper integration of many separate parts, the smallest of interruptions in one part could affect the operation and profitability of the whole plant. Bosch undertook the most fundamental investigation and proving of every single plant item, and, in most cases, it was necessary to build completely new apparatus for a particular duty. For example, it was essential that the compressors used should neither allow the valuable and flammable synthesis gas to leak out, nor allow any air to be drawn in at the suction side. The specialist compressor firms at that could not meet these two conditions, so Bosch set about solving the problem himself. In particular, it was impossible to hold a seal against rotary shafts, hence, in order to eliminate loss of gas from the circulation pumps, the blower was installed in the gas line so that only the inlet and exit lines remained to be sealed; the whole system was then completely enclosed in a strong-walled steel tube. As the bearing was inaccessible, it was necessary for the motor to run for many months at a time in an aggressive gas atmosphere; the arrangement was known as a 'mole pump', and although it astounded the machine contractors, Siemens, it worked.

Further problems which remained centred around seals, flange materials, armatures and instruments etc. Bosch required that all pieces of machinery, apparatus and events be investigated with the utmost care and precision; he later credited his ultimate success to this rigorous and fundamental way of working. On taking delivery of a piece of machinery, he was not content with proving its reliability, but demanded that it be taken apart and every piece characterised. A special laboratory was provided for these measurements.

The end of 1911 was an exciting time at Ludwigshafen. Scarcely a couple of days went by at a time without an interruption. Numerous fires occurred, and often the roar of high pressure gas flames could be heard, as a result of a rupture of a main or vessel. Fortunately, no serious accidents occurred.

One of the most difficult problems was found to be the bringing back on line of the catalytic vessel, after it had been allowed to cool for maintenance; a thick-walled steel vessel, containing catalyst and heat exchanger, had to be raised to a temperature of 770 K in a reasonable time. The first double-walled vessel had been provided with an external means of heating only. The vessel was enclosed by a case which contained hot gases, and the necessary heat input through the thick shell resulted in overheating, which became even worse when larger-sized vessels were used, thus increasing the danger to the mechanical strength of the steel during start-up. It became clear that an internal means of heating was required, and many different methods were tried during 1911, without conspicuous success. Bosch considered the idea of using inverted flames in the interior of the vessel: oxygen or air under high pressure would be burnt in the hydrogen-rich synthesis gas i.e. an oxyhydrogen flame inside the vessel was proposed. This idea did not fill his colleagues with enthusiasm, particularly when they learnt that they would have to supervise continually the burning of the flames, by observation with a sight glass; at normal pressures the flame was hardly visible, but it was established that the flame became much more visible at higher pressure, becoming bright blue. It was at this time that von Brunck, possibly worried by the dangers inherent in this form of internal heating, and impelled to examine things thoroughly, decided to make a tour of inspection of the works. Three days later, on December 4th 1911, he died, completely unexpectedly.

At that time BASF formed, with Bayer and AGFA, a group of three large chemical concerns united in a mutual partnership (Interessengemeinschaft), with the aim of protecting each other's interests. With the death of von Brunck, it was the turn of Carl Duisberg of Bayer to head the partnership, and Bosch and his team were anxious to see whether the new leadership would back the ammonia venture with as much enthusiasm as had von Brunck. Later in December, it was decided that the project to construct the ammonia factory should be expanded to twice its original size, and that Bosch should be responsible for procuring all the equipment.

More land was acquired in the vicinity of Oppau, and test boring began. Installation of essential services commenced on May 7th 1912. Bosch began the task of ordering all the machines and equipment, and his work now took on a different aspect; istead of being concerned solely with technical matters, he now had the construction of the plant to worry about. The first problem was the sandy soil, which was not solid enough to support the heavy machines, which came loose from their foundations. The scale of the exercise was awesome, with large quantities of flammable gas requiring compressing and conducting around the site safely and with as little loss as possible. There were still numerous sceptics expressing doubt as to the final success of the venture, but in autumn 1912 Bosch considered that all the necessary preparative work had been carried out successfully, and reported so to the Board, which was completely convinced of his eventual success. In September 1913, two years after the building work had begun, the Oppau works were put into operation.

G. The First Ammonia Plant at Oppau [21, 22]

The first factory was designed for a production of 30 tonnes per day of ammonia. Hydrogen, obtained from water gas by refrigeration, was passed through caustic soda solution at 473 K and 200 atmospheres pressure to remove small amounts of residual carbon monoxide, and then mixed with nitrogen from the liquefaction of air; before reaching the synthesis vessels it was passed through a heated guard vessel, a preliminary catalytic vessel which removed the final traces of catalyst poisons. The synthesis vessels themselves were 300 mm in diameter, contained 300 kg catalyst and yielded 3–5 tonnes of ammonia a day.

After a few months on line, it became apparent that the Linde refrigeration process for the production of hydrogen was unsuitable for use on such a scale; an alternative method of production of hydrogen was thus required, and work on a replacement source was undertaken in 1914. A member of Bosch's team, Dr. Wilhelm Wild, who had been a student of Nernst, developed a catalytic reaction between water gas and steam. The water gas mixture, consisting of hydrogen and carbon monoxide, on passage with steam over a heated bed of iron oxide, yielded carbon dioxide and additional hydrogen:

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

The process was exothermic and produced excess heat which could be used to generate some of the necessary steam; carbon dioxide could easily be removed from the gaseous products by scrubbing with water. The new catalytic process had the added advantage that the carbon dioxide so formed could be utilised in the subsequent manufacture of fertilisers. Bosch became convinced of the value of this method, and devoted a great deal of effort to its development.

The use of the 'water gas shift reaction' permitted the purification of a hydrogen/nitrogen *mixture*. Instead of using the Linde process for the provision of nitrogen, it was obtained by first reacting air with red hot coke to give 'producer gas', (a mixture of 60 % nitrogen and 40 % carbon monoxide), which could then be mixed with the water gas, and the carbon monoxide resulting from both sources could be converted to carbon dioxide by the catalytic reaction described above; the effluent gas from this reactor would then consist of a mixture of hydrogen, nitrogen, carbon dioxide and a small amount of carbon monoxide. The carbon dioxide could then be removed satisfactorily by dissolving in water in washing towers.

The method so far employed for the removal of residual carbon monoxide, namely by means of caustic soda solution, proved troublesome, however, as the vessels containing the alkali became badly corroded. An alternative method for the removal of carbon monoxide was investigated, which used copper liquor as the absorbent, following the method for the analytical determination of carbon monoxide. Again, the solution was found to be very corrosive, and could not be contained in iron apparatus, so it seemed that more expensive metals would have to be used. There was a danger that the whole ammonia synthesis project might falter on account of the failure to contain the copper solution, with the consequent additional cost of replacement material. Bosch set the young chemist Carl Kranch the task of finding an additive to the copper solution which would give protection against corrosion. Kranch set up a large series of corrosion tests, then went off on his summer vacation. On his return, he observed that only one sample had resisted corrosion, one which had been immersed in copper liquor mixed with a large quantity of ammonia; by the simple expedient of adding ammonia to the solution, the corrosion had been arrested, and this method of carbon monoxide removal went on to be used on the large-scale.

The remaining problems with the final purification step for the synthesis gas had been solved, and the gas leaving the copper-liquor gas-scrubbing towers should be pure hydrogen and nitrogen, in the volumetric ratio of three to one. The ratio was maintained precisely by the addition of nitrogen which had been obtained from a Linde unit.

H. The Refined Plant at Oppau [21, 22, 37]

The new catalytic 'shift' process for the removal of carbon monoxide from the reactant gases was introduced into the large scale plant in February 1915, and the Linde hydrogen facility became redundant later that year. A further improvement to the plant was made at the beginning of 1915, when a building was established dedicated to the synthesis reactors. In April, the first large-size vessel was installed; it was 800 mm in internal diameter, and 12 meters long, and was designed for a yield of 20 tonnes of ammonia per day. A photograph of one of the vessels is shown in Plate 5; the synthesis building is also shown in Plate 6.

The yield from the plant rose steadily throughout the next year, reaching 200 tonnes per day in June 1916, and peaking at 230 tonnes per day in

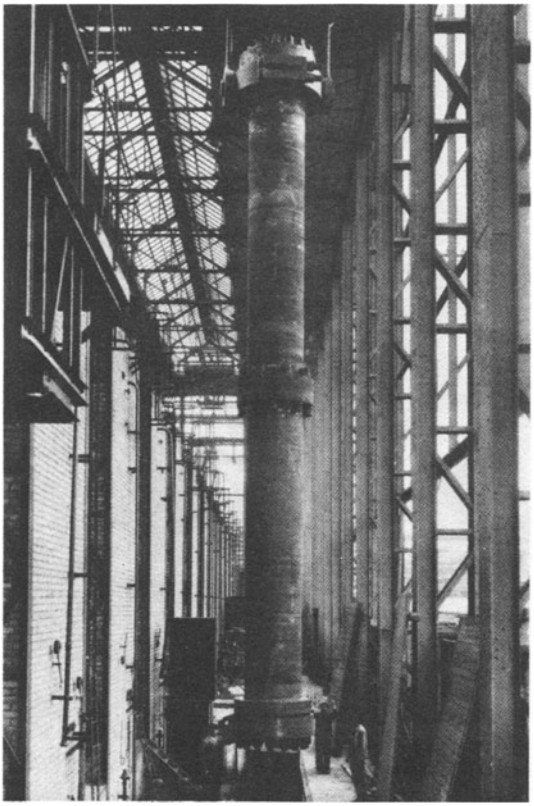


Plate 5. Large catalytic vessel for ammonia synthesis of Oppau plant. (Reproduced with permission from "Geschichte der Ammoniaksynthese", A. Mittasch, (1951), Verlag Chemie, facing p 128)

December 1917. Thereafter, a steady decrease in output was observed, due to damage caused by air attack on Oppau.

The main features of the refined plant were as follows. Water gas and producer gas were manufactured, alternately, in large generators, and the product gas streams so produced were led into gas holders, where they were allowed to mix and freed from dust by spraying with water. The mixed gas was then saturated with steam, before passing through the first catalytic vessels ('shift' reactors) where the majority of the carbon monoxide was converted to carbon dioxide and more hydrogen was generated. The exit gas was a mixture of hydrogen, nitrogen and carbon dioxide with 2% carbon monoxide. The hot gas then entered a heat exchanger where the heat evolved in the reactors was used to generate steam and saturate the incoming cold gas with water vapour, all with a saving of energy. Compression of the gas to 25 atmospheres was then effected in the first three stages of a compressor, after which the gas entered, at pressure, towers where the carbon dioxide was removed by solution in water. The carbon dioxide-containing solution was pumped to towers and then flash evaporated through turbines which were

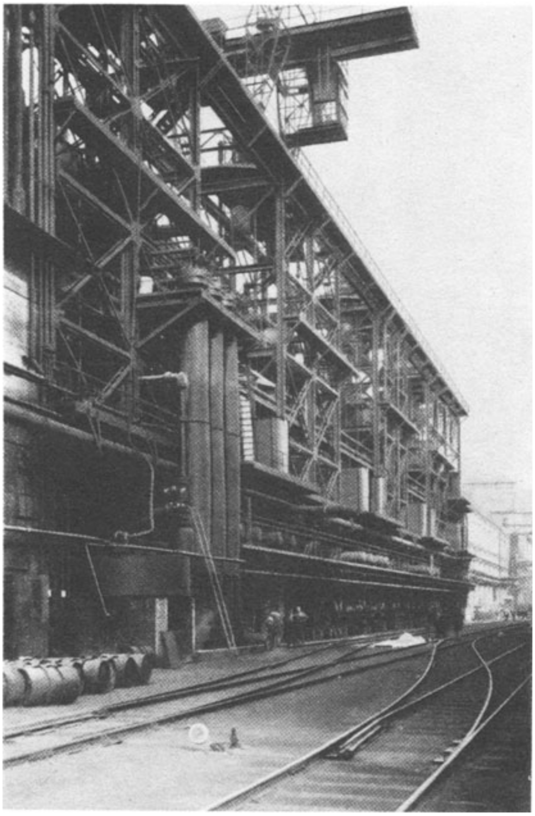


Plate 6. Ammonia synthesis area of Oppau plant. (Reproduced with permission from "Geschichte der Ammoniaksynthese", A. Mittasch, (1951), Verlag Chemie, facing p 96)

mounted on the same axle as the pumps, thus recovering half of the energy of compression. The gas, which by now was almost completely free of carbon dioxide (0.5–1.0% carbon dioxide, 1–2% carbon monoxide), was compressed to 200 atmospheres in the fourth and fifth stages of the compressor before passing into the carbon monoxide removal towers, where the carbon monoxide was absorbed in ammoniacal copper liquor; the copper liquor was regenerated by evacuation, and then returned to the absorption towers. The synthesis gas now contained about 77% hydrogen and 23% nitrogen, with only very small quantities of catalyst poisons. A stoichiometric ratio of 3:1 was obtained by adding nitrogen from a refrigeration unit. The final purification stage was then reached, in which the gas was passed through a vessel of 300 mm internal diameter and 8 meters high, heated to 623 K, containing a catalyst capable of effecting the conversion of the last traces of carbon monoxide to methane, and oxygen (from the Linde nitrogen) to water; it also removed final traces of sulphur. The gas was then introduced into the circulation system, just before the ammonia absorption stage, so that the final residues of carbon dioxide were removed, before the

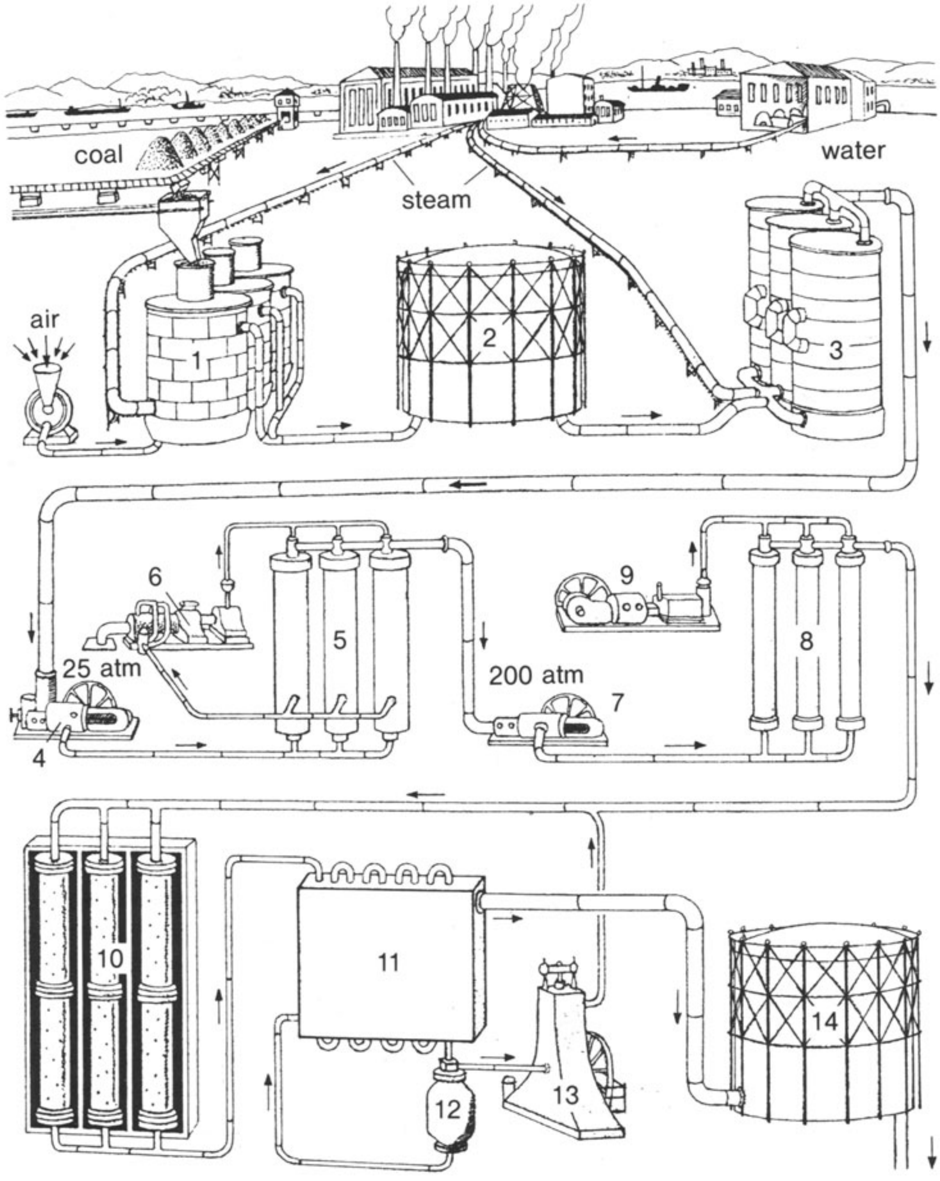


Figure 2. The BASF Ammonia Synthesis Plant at Ludwigshafen.
(Reproduced with permission from "Im Banne der Chemie, Carl Bosch, Leben und Werk", K. Holdermann, (1953), Econ-Verlag, facing p 81)
1 Production of raw gas, 2 Storage of raw gas, 3 Catalytic reactor for production of hydrogen, and removal of carbon monoxide, 4 Compressor (for production of 25 atmospheres), 5 Removal of carbon dioxide, by means of scrubbing with water, 6 Pump for high pressure water, 7 Compressor (for production of 250 atmospheres), 8 Removal of residual carbon monoxide by means of scrubbing with ammoniacal copper liquor, 9 Pump for high pressure copper liquor, 10 Ammonia synthesis reactors, 11 Condenser and evaporator, 12 Separator, 13 Circulation pump, 14 Gasholder for gaseous ammonia

fully-purified gas was finally introduced into the synthesis reactors. These 12 meter high, double-walled vessels were half-filled with about 2 tonnes of catalyst, the other half being occupied by a heat exchanger. The effluent gases then went via a circulation pump capable of dealing with 600 cubic meters of compressed gas per hour, to the ammonia absorber, where it was absorbed under pressure by a water spray. The ammonia solution was collected in large, high pressure vessels, let down into lower pressure holders and then pumped, as a 20–30% solution in water, into supply vessels. A simplified schematic diagram of the Oppau plant is shown in Figure 2.

4. Influence of the First World War on the Haber Process

The influence of the first world war on the development of the Haber process has been the subject of much debate. Some reports in the scientific journals dating from the years immediately following the war alleged that war was not declared by Germany until the success of the Haber process had been assured [38, 39], and also that the Ostwald process for the production of nitric acid from ammonia was held back from commercial exploitation by the German authorities as a strategic asset [40]. Claims were also made that the Haber process was developed with government aid, finance being made available for extensive and secret research [41, 42]. The available evidence [43, 21], however, reveals a rather different story.

Before the declaration of war, Germany had relied on Chilean nitrates to make up half her annual requirement of fixed nitrogen. These supplies were cut off in August 1914, however, and as the statistics of German nitrate imports for the previous few years reveal, no attempt had been made to build up a strategic reserve. It was apparent that the German authorities had not fully appreciated the implications of a sea blockade, as, in September that year, Professors Haber and Emil Fischer had deemed it necessary to draw the attention of the War Ministry to the situation. Soon afterwards, Fischer submitted a report to the authorities, detailing the required action to be taken to ensure that stocks of nitric acid would be available for explosives manufacture. A very small Ostwald ammonia oxidation unit existed in Gerthe, in the Ruhr, but its capacity was slight and it relied on the use of the precious metal platinum as a catalyst. The government decided to support the development of the Ostwald process, and Bosch, at BASF, became involved in this work. He had already been summoned to the War Ministry in September 1914, and had been alarmed at the lack of awareness of the importance of fixed nitrogen to the success of military operations.

By working night and day, Bosch, Mittasch and Lappe developed a cheaper catalyst, based on iron-manganese-bismuth oxide, and an improved reactor, for the Ostwald process, and, by May 1915, this new unit at BASF was producing nitric acid, using raw material ammonia produced by the Haber process. The oxidation unit at Gerthe was enlarged, and further Ostwald units built elsewhere, all of which used ammonia obtained as a by-product from coke ovens. This usage of ammonia for military purposes meant that less was available for agricultural use, and the government decided to give financial support to operators of the cyanamide process, since the product obtained could be used directly as a fertiliser.

It was decided, late in 1914, that although the Oppau works had been designed for the production of the fertiliser ammonium sulphate, agricultural fertiliser manufacture would cease for the duration of the war, ammonia liquor and sodium nitrate becoming the more important products for military purposes. Despite the Oppau plant's increased production during 1914 and 1915, it became apparent to the authorities, towards the end of 1915, that more capacity was required. Bosch was again summoned to the War Ministry, and the proposal was put forward that BASF should enlarge their facility for the production of ammonia. All the development costs of the Haber process so far had been borne by BASF and its partners; BASF had paid for all the original research and pilot plant work itself, and the Oppau plant had been financed jointly by the Interessengemeinschaft of BASF, Bayer and AGFA, purely as a commercial venture. The enlargement of the synthetic ammonia facility was too great a financial burden for BASF, so the government decided to transfer its financial support from the cyanamide process to the Haber process, and a loan was arranged in April 1916.

Since Oppau had already suffered some damage by air attack, it was decided not to enlarge the existing plant, but to build another plant at a less-vulnerable site. The small town of Leuna, in the east of Germany, was chosen. It had the advantages of being on the main railway line from Frankfurt (am Oder) to Berlin, and having readily-available supplies of water and brown coal nearby. Despite numerous problems during construction, including extremely bad weather and shortage of materials, the first ammonia was produced at the new plant on April 27th 1917, only eleven months after building work had started. The design of the new plant incorporated all the improvements made to the Oppau plant, and its capacity, when complete, was 250 tonnes of ammonia per day. On completion, plans were put forward for the enlargement of capacity to over 400 tonnes per day, and by the end of the war the Oppau and Leuna works were capable of producing, respectively, 50,000 and 130,000 tonnes of fixed nitrogen a year. Though they never achieved full capacity because of shortages and interruptions due to the war, they did provide, in 1918, half of Germany's requirement for fixed nitrogen. This statistic is especially impressive when compared with the contribution of the Oppau plant at the beginning of the war; the first Haber plant had the capacity then to supply about 3 % of Germany's needs, although it never actually produced at full capacity.

Thus, whilst it is extreme to suggest that the Haber process was a decisive factor in the declaration of war, there is no doubt that the war had a profound influence on the development of the Haber process, to the extent that it did ultimately play a significant role in the later years of hostilities. The scale of operation increased from a small, and still somewhat experimental, unit in 1913, to an extensive facility based on two sites, and capable of producing twenty-five times as much, by 1918. Without this capacity, the war would almost certainly have ended at an earlier date.

5. Developments Outside Germany [37, 44, 45]

During the war, other nations did not suffer shortages of fixed nitrogen to the same extent as did Germany. Britain was able to produce large quantities of by-product ammonia from her town's gas industry, sufficient to supply her allies' as well as her own requirements for nitrates of military value, thanks to an indirect process, developed by Brunner Mond and Company, for the production of ammonium nitrates from ammonium compounds and Chilean nitrates. Nevertheless, extensive work was carried out in many countries, with the aim of producing synthetic nitrogen compounds.

In Britain, the Munitions Inventions Department set up a team of research workers to investigate methods for the synthesis of ammonia and its subsequent oxidation; in charge of this work was H. C. Greenwood, who had studied with Haber at Karlsruhe. A team with similar aims existed in France, but by the end of the war neither had progressed anywhere near a viable process. In the U.S.A., the government had supported work on the synthesis of ammonia by the Haber and Cyanamide processes, but it was a commercial organisation that made the first progress in this area. A small, experimental catalytic ammonia unit had been developed by the General Chemical Company in Long Island, using a process similar to that of BASF, but using a different catalyst (a cobalt-sodium catalyst was used). Interest in the Haber process had first been aroused in the U.S.A. when Professor Bernthsen of BASF had given a paper [46] there in 1912. After the entry of the U.S.A. into the war, the fixation of nitrogen came under military control, and two plants were planned, one to be based on the General Chemical process, the other to be a cyanamide plant; the economics of the Haber process, as compared with other nitrogen fixation methods, were not known outside Germany at that time, so the cyanamide process was still to be reckoned with. The catalytic plant was built at Muscle Shoals, Alabama, but was not successful, producing only a small quantity of ammonia; the process was not sufficiently well-developed when taken to full-scale, and the catalyst was found to die off very rapidly. It was later developed to commercial scale, with a much more active catalyst which lasted far longer than the original one, and the first successful plant was commissioned in Syracuse, New York, in 1921. Meanwhile, a research facility, the Fixed Nitrogen Research Laboratory, was established by the authorities, so the foundations for the development of an American ammonia industry had been laid.

Although the team supported by the French government had not made much progress by 1918, an advance had been made by the French engineer Georges Claude. He developed a modified Haber process, which operated at much higher pressure (1000 atmospheres), making the separation of the ammonia product much easier. A higher conversion per pass was also obtained. After successful trials of this process in Paris in 1919, Grande Paroisse erected a full-scale plant in the 1920s. Also, in 1919, the French Minister of Industrial Reconstruction signed a convention with BASF for assistance with regard to the technical details for the economic working of the Haber process, enabling the Kuhlmann company to exploit the BASF patents obtained by the French War Minister under the terms of the Peace Treaty.

The British government had intended to build a Haber synthetic ammonia plant, and had bought a site at Billingham, in the north-east of England, for this purpose. At the end of the war, government support ceased, and the project was put up for sale. The Brunner Mond company considered taking it over, but, like the Americans, were unsure of the economics of the Haber process; at that time, it was not known whether fixed nitrogen from this process could compete with Chilean nitrate on cost. Directors of Brunner Mond wished to inspect the BASF plant, and in April 1919 embarked on a mission to Oppau [42, 45], hoping to obtain such detailed information as would enable the design, construction and operation of a similar plant in Britain. BASF were extremely unhappy at this prospect, and informed their employees that if they divulged any information they would be dismissed; as the plant was in the French sector, BASF also informed the French of their threat to close the plant, making 10,000 workers idle and leaving the French authorities to cope with the situation. The British mission received no cooperation. The plant was shut down during the visit, dials and gauges being blacked out or removed, ladders and stairs taken away, and maker's names removed from machines. All employees stopped work immediately the British entered the buildings. No sketches were permitted on the premises, so these had to be made afterwards from memory. Despite all these problems, a detailed report was written, but it was stolen by the resourceful and determined expedient of sawing through the bottom of the guarded railway wagon in which it had been stored. Fortunately, one member of the mission, Captain Cowap, had kept a set of duplicate drawings, and the report could be rewritten on returning to England. After carfully considering the economic viability of the process, Brunner Mond decided to acquire the Billingham site, and also obtained the rights granted to BASF under British Patent, which had been confiscated during the war. A plant was planned to produce 20 tonnes per day of ammonia and 10 tonnes of nitric acid, and the new company formed to progress the plan, Synthetic Nitrates and Ammonia (later to be one of the founders of Imperial Chemical Industries), began work on the biggest project so far undertaken by any British chemical firm. Research work was initiated on all aspects of the process, and problems similar to those encountered by BASF were met and overcome. Eventually, and with the help of two engineers who had worked at both BASF plants, coal-based ammonia plants were established in Britain, using the same basic technology as that developed in Germany.

The Haber process, in several variations, became established in many countries during the 1920s. The process represented a significant technical advance over the fixation of nitrogen by the earlier methods. The energy requirement of the new catalytic process per tonne of fixed nitrogen was considerably less than for alternative processes, and so further development of the electric arc and cyanamide technologies ceased.

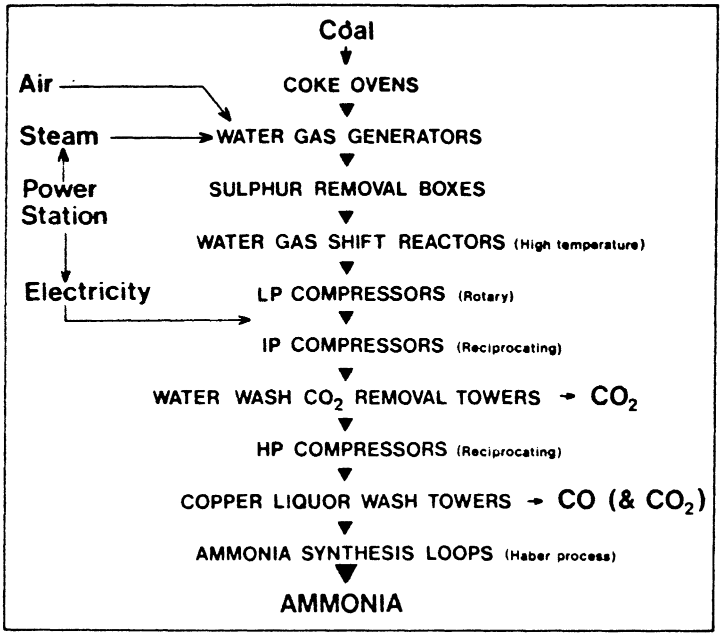
6. Developments in Ammonia Technology [47, 48]

Between the 1920s and the 1950s, the major changes taking place in the synthetic ammonia industry were related to size. The technology upon which the plants were based changed very little from that originally developed by BASF, but the world capacity for the production of ammonia increased. A greater number of plants were built, and existing units were enlarged, generally by adding parallel streams of similar equipment. Since the 1960s, however, ammonia production has undergone a major change, as a result of improvements in technology. Instead of multiple parallel streams with numerous interconnections to maximise use of equipment, the new plants were based on the concept of large, reliable single streams, involving lower capital and operating costs. In addition, instead of regarding the plant as consisting of essentially unrelated, but linked, individual units, integration of the whole plant was effected in order to make the most effective and efficient use of all its parts; energy generated as a result of one part of the process was recovered, to be used elsewhere in another part of the plant. This concept of large, integrated single stream plants became a reality because of the coming together of several individual advances in technology.

Plants continued to be based on coal, with hydrogen generated via the water gas reaction, until the 1950s, when, in the U.S.A., plants based on natural gas feedstocks were commissioned. The use of the methane steam reforming process, which originated from work carried out at BASF in the 1920s and which was further developed by I.C.I. in the 1930s, permitted significant reductions in the capital cost of plant. Also, in 1962, a process developed by I.C.I. at Billingham made possible the production of synthesis gas from light naphthas, whereby the plant simplifications made possible by the natural gas steam-reforming process became available at sites which did not have a ready supply of natural gas. Further simplification resulted from the replacement of the water-wash method for the removal of carbon dioxide by a process using aqueous solutions of potassium carbonate or monoethanolamine, which were much more efficient for this purpose. Development of a low temperature water gas shift catalyst, and the installation of a methanator, enabled the elimination of the copper liquor stage for the removal of carbon monoxide, while advances in pressure vessel technology enabled larger and larger synthesis converters to be used. The most important advance in the engineering aspects of the plant, however, was the development of large centrifugal compressors which could assume the duties previously carried out by reciprocating machines. Although less efficient, the centrifugal compressors cost less, occupied less space and were more reliable than the older machines; less maintenance was required and, more significantly, the centrifugal machines could be driven by steam generated elsewhere on the plant.

The concept of integrated plant design was pioneered by the Kellogg Company, and the first three 900 tonne per day plants in the world were built at I.C.I. in Billingham. Plants such as these rapidly rendered the older, smaller units obsolete. The attached flowsheets (Figure 3), show a comparison of the old coal-based process and the new process based on natural gas.

Coal based route to Ammonia (Old technology)



Modern route to Ammonia

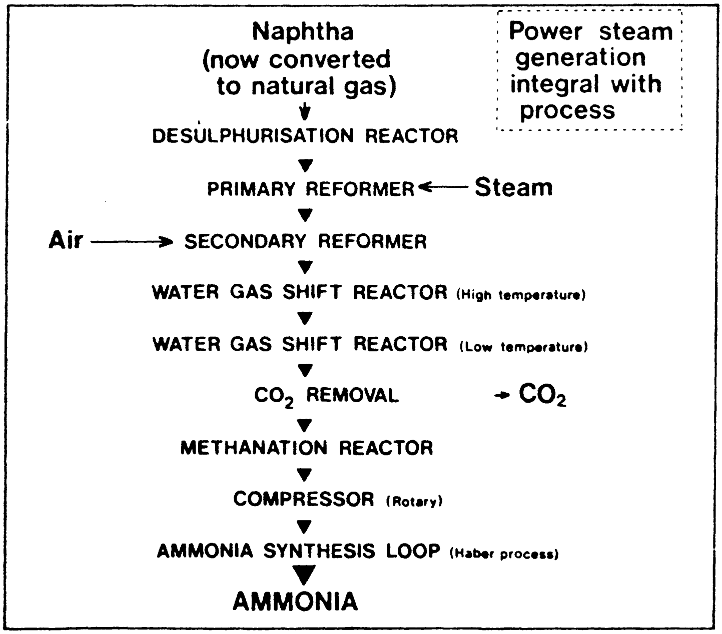


Figure 3. Comparison of old and modern routes to ammonia at Billingham

Whereas the older plants required a power station for the provision of electricity and steam, this is no longer necessary, as the steam required to drive the compressors in the newer process is generated on the plant itself.

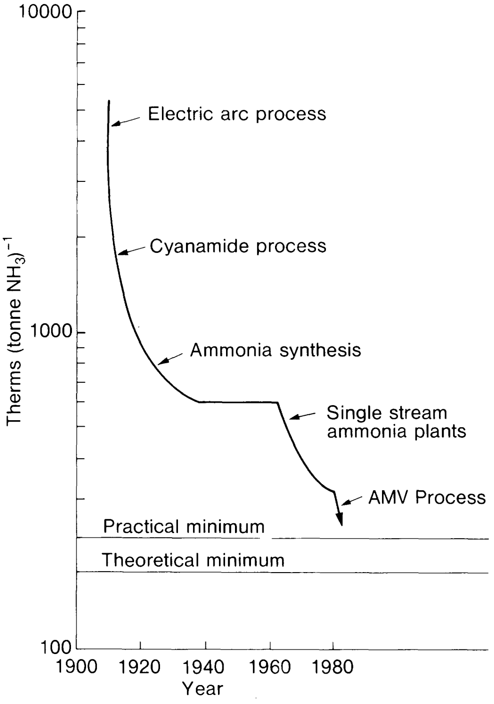


Figure 4. Efficiency of nitrogen fixation

The accompanying graph (Figure 4) shows the cost of fixing a tonne of nitrogen as a function of time. The electric arc process required a colossal 6800 therms for every tonne of nitrogen fixed. The cyanamide process was still more than four times less efficient than a modern ammonia plant, demanding 1800 therms per tonne of ammonia produced. The revolution brought about by the advent of single stream plants is apparent as a step change in efficiency on the graph. Since then, the curve has continued to approach the minimum practically achievable, but in the 1970s this has been accompanied by a gradual rise in the capital cost of equipment. In 1982, a new, energy-saving process was announced by I.C.I. Agricultural Division [49], which permits an even closer approach to the minimum practical expenditure of energy to form a tonne of ammonia. This new process allows efficiency gains together with reduced capital cost, and uses an improved synthesis catalyst, which permits the use of lower pressures in the synthesis loop (80 atmospheres).

Although seventy years have elapsed since the first catalytic ammonia plant made ammonia, it is still possible to make significant improvements to the process.

7. Epilogue

The preceding account has shown that Sir William Crookes' prophesy, that the chemist would ultimately solve the problem of providing a replacement for the finite natural reserves of fertiliser, has been fulfilled.

Haber had originally thought the technical exploitation of such a process unlikely, based on his original (and over-optimistic!) data on the position of the ammonia equilibrium. When prompted to reconsider his experimental results, by the criticisms of Nernst, who actually made the first synthetic ammonia at pressure, Haber's interest in the technical synthesis was reawakened, and he then carried the ideas through to a successful prototype stage. It was thus Haber who laid the foundations for the technical synthesis of ammonia from its elements.

The development of the ideas of Haber to fruition on the large scale was, however, due to Bosch, and his achievements in the space of just a few years cannot be overestimated. Bosch considered, with hindsight, that the solving of the problem of the high pressure catalytic vessel was the vital stage in this work and remarked how surprising it was how, "after months and years with a problem, overnight the brain can provide, subconsciously, the final correlation".

In 1919, Haber received the Nobel Prize for his work related to the catalytic synthesis of ammonia. The same distinction was afforded to Bosch in 1931, for his contributions in the development of high pressure technology.

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