



The discovery of the process for economically viable manufacture of ammonia came at an almost *providentially selected time* in human civilization. The post industrial revolution period was witness to some drastic demographic changes, which lead to regions of dense human population that relied heavily for its food production on sparsely populated regions. This caused one of the earliest impacts of human civilization on the environment – nature's 'Nitrogen Cycle' had been meddled with, and the soil needed to be artificially replenished of its rapidly depleting amounts fixed nitrogen for sustained agricultural utilization. Haber's Nobel Lecture beautifully brings to fore the issues that concerned scientists at the turn of the last century and the importance of his discovery. In hindsight, one wonders how the human population would have made it this far had it not been for Haber's discovery.

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The synthesis of ammonia from its elements

Nobel Lecture, June 2, 1920

Fritz Haber

The Swedish Academy of Sciences has seen fit, by awarding the Nobel Prize, to honour the method of producing ammonia from nitrogen and hydrogen. This outstanding distinction puts upon me the obligation of explaining the position occupied by this reaction within the subject of chemistry as a whole, and to outline the road which led to it.

We are concerned with a chemical phenomenon of the simplest possible kind. Gaseous nitrogen combines with gaseous hydrogen in simple quantitative proportions to produce gaseous ammonia. The three substances involved have been well known to the chemist for over a hundred years. During the second half of the last century each of them has been studied hundreds of times in its behaviour under various conditions during a period in which a flood of new chemical knowledge became available. If it has not been until the present century that the production of ammonia from the elements has been discovered, this is due to the fact that very special equipment must be used and strict conditions must be adhered to if one is to succeed in obtaining spontaneous combination of nitrogen and hydrogen on a substantial scale, and that a combination of experimental success with thermodynamic considerations was needed.

It was particularly significant that earlier attempts had not succeeded, even fleetingly, in achieving with absolute certainty a spontaneous union of nitrogen and hydrogen to form ammonia. This gave rise to the prejudice that such a production of ammonia was

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impossible, and in the course of time this enjoyed considerable support in chemical circles. Such prejudice leads one to expect pitfalls which, far more than clearly defined difficulties, deter one from becoming too deeply involved in the subject.

A narrow professional interest in the preparation of ammonia from the elements was based on the achievement of a simple result by means of special equipment. A more widespread interest was due to the fact that the synthesis of ammonia from its elements, if carried out on a large scale, would be a useful, at present perhaps the most useful, way of satisfying important national economic needs. Such practical uses were not the principal purpose of my investigations. I was never in doubt that my laboratory work would produce no more than a scientific confirmation of basic principles and a criterion of experimental aids, and that much would need to be added to any success of mine to ensure economic success on an industrial scale. On the other hand I would hardly have concentrated so much on this problem had I not been convinced of the economic necessity of chemical progress in this field, and had I not shared to the full Fichte's conviction that while the immediate object of science lies in its own development, its ultimate aim must be bound up in the moulding influence which it exerts at the right time upon life in general and the whole human arrangement of things around us.

Since the middle of the last century it has become known that a supply of nitrogen is a basic necessity for the development of food crops; it was also recognized, however, that plants cannot absorb the elementary nitrogen which is the main constituent of the atmosphere, but need the nitrogen to be combined with oxygen in the form of nitrate in order to be able to assimilate it. This combination with oxygen can start with combination with hydrogen to form ammonia since ammonium nitrogen changes to saltpetre nitrogen in the soil.

Under natural conditions the soil does not lose its fixed nitrogen. Green plants use it to synthesize complicated substances without changing it into elementary nitrogen. Animals and humans ingest it with the plants and return it to the soil in fixed form in their excretions and finally with their deceased remains. Putrefaction and combustion does destroy a certain amount of fixed nitrogen, but Nature makes good the loss when, during thunderstorms, lightning combines nitrogen and oxygen in the upper layers of the atmosphere, which is then washed down by the rain. To this nitrogen-fixing action of electrical discharge as a source of bound nitrogen is added the activity of soil bacteria, some of which live free while others are to be found settled in the root nodules of many plants, converting free nitrogen into bound nitrogen.



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Agricultural husbandry essentially maintains the balance of bound nitrogen. However, with the advent of the industrial age, the products of the soil are carried off from where the crops are grown to far-off places where they are consumed, with the result that the bound nitrogen is no longer returned to the earth from which it was taken.

This has caused the world-wide economic necessity of supplying bound nitrogen to the soil. This need is increased by national economic considerations, which, with the denser population of industrialized countries, call for increased agricultural productivity at home, and it is yet further increased by the fact that expanding industry requires fixed nitrogen for many of its own chemical purposes. The demand for nitrogen, like that for coal, indicates how far removed our way of life has become from that of the people who themselves fertilize the soil they cultivate.

Agriculture, always the main consumer, is not satisfied with a supply of nitrogen alone – potash and phosphates* are equally indispensable – but the world possesses far fewer natural resources for meeting nitrogen requirements. And so, naturally, concern over nitrogen supplies has become the first of the great obstacles that lie along the highway of world commerce upon which we have been travelling in recent decades.

The combining of nitrogen with hydrogen to form ammonia as with oxygen to produce nitrates had already occupied science and, to some extent, technology. Combination with hydrogen directly from the elements had been induced by various forms of electrical discharge, which of course resulted in an energy consumption of alarming proportions. Indirect combination, on the other hand, had been developed with remarkable technical results; the nitrogen was combined with other elements and this combination was then hydrolysed with water whereby ammonia was split off. Only the spontaneous association of the elements was unknown when, in 1904, I began to occupy myself with the subject; it was held to be impossible after pressure, heat, and the catalytic action of platinum sponge had been found unable to produce the effect.

The more tightly knit nitrogen molecule does not break down as easily as oxygen, the next element in the periodic system. The abundant examples we have of autoxidation are thus matched by a complete lack of spontaneous reaction of elementary nitrogen in the inanimate world at normal temperatures. The inaccessibility of nitrogen nullified all the many efforts made to develop a technical ammonia process.

In only one respect has the study of indirect methods of synthesizing ammonia from the elements been able to get round the difficulties. Frank and Caro obtained the important



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calcium cyanamide through the action of nitrogen on calcium carbide obtained from lime and coal in the electric arc. Splitting the calcium cyanamide with water produces ammonia, and the process takes place in the soil without any particular help from us, once the cyanamide has been added to the soil as fertilizer. The saving in factory processing achieved by this, plus the fact that the only raw materials required are lime, coal and nitrogen, have been important factors in the establishment of the process.

Efforts to combine nitrogen with oxygen go back further than those aimed at combining it with hydrogen. The basic fact of the combination of nitrogen with oxygen during sparking had already been observed by Cavendish and Priestley. In this case the first product is nitric oxide, which converts to nitric acid in a spontaneous reaction with oxygen and water. The nitric oxide synthesis is a process requiring heat, and unless energy is supplied can, for thermodynamic reasons, only occur spontaneously to any appreciable extent at extremely high temperatures. However, the supply of energy required at normal temperatures is so small that disadvantage of having to provide it is outweighed by the advantage of needing only air and water as raw materials.

Installations on a considerable scale were built in a number of places and the method was evidently well suited to making use of the vast supply of energy which could be derived from waterfalls for chemical purposes; but this method of synthesizing nitrogen has still not reached the levels of production which it appeared to promise. Its progress is limited by the fact that with a consumption of one kilowatt-hour no more than 16 grams of nitrogen are converted into nitric acid, whilst a complete conversion of electrical to chemical energy ought to yield 30 times as much.

The formation of nitric oxide is determined, and limited, by thermal conditions in the arc and its surroundings. Determination of the thermodynamic equilibrium of nitric oxide synthesis by Nernst confirmed this explanation. An extrapolation of his experimental results and the best figures for the specific heat of the gases involved up to the temperature of 3,000°C or 4,000°C led to the remarkable conclusion that more than 1½ times or twice the technical yield per kilowatt-hour could still not be achieved when no reformation of nitric oxide in the cooling circuit occurred at all. The source of the low yield lay in the fact that the heating of a large air mass at very high temperatures enabled only a small fraction to convert thermodynamically to nitric oxide. In spite of the fact that, for a variety of reasons, this calculation cannot pretend to considerable accuracy, its result obviously approaches the truth. Practical experience has shown that no worthwhile saving of energy can be achieved by heat regeneration, manifestly because the deterioration of the quench-



ing action involved militates against this. It is impossible to do away with the arc discharge without deviating from the basic processes which comply with the requirements of mass production.

There were proposals to utilize the explosive reactions simultaneously in a motor and as a source for the synthesis of nitric oxide. I myself placed no faith in the linking of two such widely-differing functions. Yet the utilization of the heat of flame gases appeared to me to be not incompatible with the formation of nitric oxide, and worthy of closer investigation. This has been extended over the flames of carbon monoxide, hydrogen and acetylene. It was found that corresponding to 100 molecules of the main products of combustion, carbon dioxide and hydrogen, 3 to 6 molecules of nitric acid could be obtained. In the case of carbon monoxide and hydrogen this required increased pressure. Carbon monoxide had the advantage over the hydrogenated gases, since the presence of water vapour in the hot products of combustion favoured the reversion of the nitric oxide in the elements along the cooling circuit. With this gas the molecular nitric oxide: carbon monoxide ratio could easily be brought, with air, to 3 : 100 and with a mixture rich in oxygen to double that ratio. For technical utilization however, these values were not sufficient incentive; the weight, which declined on the direct combining of nitrogen with hydrogen, therefore again underwent an increase.

I have not pursued further the combining of nitrogen and hydrogen by corona discharge and by sparking. It seemed certain to me that this method would not prove itself to be the most advantageous. In the final analysis the assessment of each method rests upon the ratio between the energy consumed and the yield, in other words, between coal consumption and nitrogen yield (the consumption of hydraulic power being reckoned as the equivalent consumption of coal).

Nothing seemed less hopeful, though, than the thought that the enforced combining of nitrogen with hydrogen could be achieved with so little energy that one would have spare energy left over for the production of hydrogen. There remained merely the possibility of discovering the requirements for spontaneous formation of ammonia from the elements. The positive heat of formation of ammonia indicated that such a synthesis might be achieved without the assistance of electrical energy. Against this there was the fact that neither Deville nor Ramsay and Young had obtained ammonia by heating nitrogen and hydrogen.

I therefore began tentatively to determine the approximate position of the ammonia equilibrium in the vicinity of 1000°C. It now transpired that earlier trials had only proved



negative by accident; it was easy, in the vicinity of 1000°C and using iron as a catalyst, to obtain the same ammonia content from both approaches. The results of individual experiments fluctuated between 1/200% and 1/80%, and some discrepant values seemed to me to point to the upper limit as the probable value; later more precise data proved the lower limit to be the correct figure and showed the origin of the higher values to be in the properties of the catalysts, which when fresh temporarily bring about the synthesis of surplus ammonia.

It was further shown that the same results could be obtained with nickel as with iron, and it was found that calcium and in particular manganese were catalysts which would bring about a combination of the elements even at lower temperatures. At 1000°C the rate of reaction was adequate with a small amount to produce continuously a comparatively large quantity of ammonia. By having a circulation system which alternately brought the gas at high temperature in contact with the metal and then washed out the ammonia at normal temperature, the conversion of a given mass of gas to ammonia could proceed stage by stage.

By determining results at a given pressure, temperature and initial mixture of nitrogen and hydrogen, the state of the theory allowed obtainable results to be approximately predicted for optional temperatures, pressures and mixtures of nitrogen and hydrogen. In the light of the formula, it was possible at once to foresee the increase of attainable maximum content with decreasing temperature, its proportional relationship with the gas pressure, and the fact that a mixture of 3 parts of hydrogen to 1 part of nitrogen must result in the highest ammonia content.

The most important point realized at that time was that from the beginning of red heat onwards no catalyst will produce more than a trace of ammonia from the most favourable gas mixture at normal pressure, and that even at greatly increased pressure the point of equilibrium must continue to be very unfavourable. If one wished to obtain practical results with a catalyst at normal pressure, then the temperature must not be allowed to rise much beyond 300°.

At that point it seemed to me, in 1905, useless to pursue the problem further. A combination of the elements had certainly been achieved, and the requirements for large-scale synthesis had been outlined; but these requirements appeared so unfavourable that they deterred one from a deeper study of the problem. The discovery of catalysts which would provide a rapid adjustment of the point of equilibrium in the vicinity of 300° and



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at normal pressure seemed to me quite unlikely: and they have not been found anywhere in the 15 years that have since elapsed.

The synthesis of ammonia which had been demonstrated at normal pressure could be carried out at high pressure on a laboratory scale without any great difficulties. It needed only a slight modification of the pressure oven, such as that used by Hempel 15 years earlier to carry out nitrogen absorption in the case of indirect ammonia synthesis under pressures of up to 66 atmospheres. But I did not think it worth the trouble; at that time I supported the widely-held opinion that a technical realization of a gas reaction at the beginning of red heat under high pressure was impossible. Here the matter rested for the next three years.

During the course of further investigations, together with my young friend and co-worker Robert le Rossignol, whose work I would like to mention here with particular sincerity and gratitude, I took up once again, in 1908, the problem of ammonia synthesis abandoned three years earlier. Immediately prior to this I had become acquainted with the technical processes in the liquefaction of air, and had simultaneously caught a glimpse of the formate industry, which caused flowing carbon monoxide to act upon alkali under heat and increased pressure, and I no longer considered it impossible to produce ammonia on a technical scale under high pressure and at high temperature. But the unfavourable opinion of colleagues taught me that an impressive advance would be needed to arouse technical interest in the subject.

To begin with, it was clear that a change to the use of maximum pressure would be advantageous. It would improve the point of equilibrium and probably the rate of reaction as well. The compressor which we then possessed allowed gas to be compressed to 200 atmospheres, and thus determined our working pressure which could not easily be exceeded for any very large series of experiments. In the neighbourhood of this pressure, the catalysts, with which we had become familiar in the course of our equilibrium determinations, very easily provided a rapid combination of nitrogen and hydrogen at above 700°C; this applied notably to manganese, followed by iron.

To achieve impressive results, however, we needed to discover catalysts which would induce rapid conversion at between 500° and 600°C. We hit upon the idea of searching the sixth, seventh and eighth groups in the Periodic System, whose principal metals chromium, manganese, iron and nickel possessed very definite catalytic properties, for metals which acted even more favourably; these we found in uranium and osmium. At the same time we discovered in osmium an excellent example of the extent to which the perfor-



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mance of a catalyst depends on its composition. When used at 200 atmospheres, both requirements which we deemed necessary to a technically-convincing conduct of the experiment, were met; the first concerned the ammonia content, the second the amount of ammonia produced per cubic centimetre of contact space per hour.

With a content of about 5% the circulation process described in 1905 was no longer a description of a method of synthesis, but a means of manufacture. With a yield of several grams of ammonia per hour per cubic centimetre of heated high-pressure chamber the dimensions of the chamber could be made so small that we felt the objections from the industry must disappear.

Finally we needed an improvement in the circulation system which could act as model for technical realization; separating the synthesis of ammonia and its removal from the flow of gas by means of reducing the pressure was not a suitable method. The cycle of ammonia production and removal must clearly be achieved by the simplest possible means at a constant high pressure. It seemed essential that the heat produced during the synthesis of ammonia should be removed from exhaust gases, where it had only a deleterious effect, and be led to the fresh gas so that the process itself yielded the heat required for its operation. The construction and operation (carried out in collaboration with Robert le Rossignol) of a small-scale plant which suited these requirements, together with the performance of the new catalysts mentioned, was indeed sufficient to persuade the "Badische Anilin- und Soda-fabrik" which thus far had devoted its attention to the indirect method of producing ammonia by means of the nitrides of aluminium, silicon and titanium, to undertake high-pressure synthesis from the elements.

The company then studied the catalysts on a large scale, using far more substantial means, and discovered ways, in the temperature employed in their production plant and particularly in the deliberate use of inert materials, of improving the performance of poor catalysts to the level of osmium and uranium. Their results were, indeed, important in the case of the classic ammonia catalyst employed by Ramsay and Young, namely iron. They also discovered an improvement in the design of the oven which overcame the effect of hydrogen on the carbon content of steel which they had observed over a long period of operation.

Present-day industrial working pressures in the vicinity of 200 atmospheres, a working temperature of about 500-600°C, circulation under constant high pressure, and the method of heat exchange from exhaust to inlet gas are all main features of laboratory work which have been retained.



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Recently Claude has announced an improvement of the process in the application of higher pressures. The pressure range around 200 atmospheres was originally chosen since it represented the limit of easily attainable levels at the current stage of development in compressor technique. In subsequent experiments Mr. Greenwood and I have gone as far as 370 atmospheres. An increase in pressure is basically only of interest if it considerably reduces the temperature of rapid conversion without creating fresh technical difficulties.

From detailed studies of the equilibria, it was seen that the change from normal pressure to 200 atmospheres creates favourable equilibrium conditions – existing between 200° and 300°C – at a temperature 300°C higher, which stimulates more greatly the activity of the catalysts. Why a higher temperature is needed is a question which we must leave to a more enlightened period of science to answer. The heterogenous catalysis of the gas reactions is a process which in the initial phase apparently represents an electrodynamic distortion of the molecule by the atomic fields at the boundary of the solid catalyst material with the gas space; it is thus a phenomenon from a field of molecular physics into which Stark's discovery had just given us a first glimpse.

The synthesis of ammonia from the elements is a result which physical chemistry was bound to reach. The notion of the reversibility of the breakdown of ammonia was already held by Deville, Ramsay and Young, and by 1901 Le Chatelier had already given thought to the effects of temperature and pressure. Failure of the first attempts at synthesis however led him to abandon the matter and to publish his deliberations only in the obscurity of a French patent taken out under a foreign name. This only came to my notice a long time after the successful conclusion of my experiments.

The solution to the problem which has been found assumes its importance from the fact that very high temperature levels are not employed and that this makes the ratio of coal consumption to nitrogen production more favourable than is the case with other processes. Results are enough to show that, in combination with other methods of nitrogen fixation which I have mentioned, they relieve us of future worries caused by the exhaustion of the saltpetre deposits that has threatened us these 20 years.

It may be that this solution is not the final one. Nitrogen bacteria teach us that Nature, with her sophisticated forms of the chemistry of living matter, still understands and utilizes methods which we do not as yet know how to imitate. Let it suffice that in the meantime improved nitrogen fertilization of the soil brings new nutritive riches to mankind and that the chemical industry comes to the aid of the farmer who, in the good earth, changes stones into bread.

