Fritz Haber: ammonia synthesis, poison gas and the Great War

A century ago Fritz Haber developed the process that is among the world's most important: the direct synthesis of ammonia, which provides abundant nitrogenous fertilisers that sustain our population. Another legacy was his activities in chemical warfare.

Introduction

Nitrogen is essential to life and abundant in air, but chemically inactive, and animals generally can only ingest it in plant form. Plants fix nitrogen, producing crops necessary for consumption, but they gradually deplete the soil of nitrogen salts.

Throughout the 19th century Chile provided more than 60% of the world's supply of nitrogen salts as saltpeter ($NaNO_3$). In 1898 the English chemist Sir William Crookes warned that such sources were diminishing and the world's population faced widespread famine unless another suitable nitrogen supply could be found.

Within a decade the German chemist Fritz Haber demonstrated an effective route for the production of ammonia from its elements.[1,2] Today about 100 million tonnes is produced annually and it is estimated that about 40% of nitrogen atoms in our bodies have been through a Haber–Bosch process reactor.[3]

Early fixation processes

Coal commonly contains about 1–2% nitrogen and during carbonisation the volatile matter liberated includes significant amounts of ammonia. Thus coke manufacture for the steel industry produces ammonia, which absorbed into sulfuric acid produces ammonium sulfate, an important fertiliser. However, yields are relatively small.

Crookes and others noticed that nitric oxide formed when an electric arc was passed through air. This route to nitric acid was suggested by scientist Kristian Birkeland and industrialist Sam Eyde, becoming the arc process, and a nitric acid plant was built (1902) at Niagara Falls, NY, but it failed. In Norway arc process plants were built producing 42 000 tonnes per annum of acid by 1925, but power consumption was high and acid yields low (2–3%).[4] Eventually costs made the process unsustainable.

Meanwhile in Germany (1904) Adolph Frank and Nikodem Caro* developed a route to ammonia synthesis. It is an indirect, high-temperature method (1000–1100°C) that reacts nitrogen with calcium carbide (from lime and coal) to form calcium cyanamide, $CaCN_2$; hydrolysis yields ammonia.

$$CaC_2 + N_2 \rightarrow CaCN_2 + C$$
$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3$$

The process was used in Germany, Italy and Norway and by 1921 about 500 000 tonnes per annum of ammonia were being produced.[4] Eventually it was overtaken by the direct method, estimated to be about 15% more cost effective (see www.nobelprize.org). In 2002 it was still being used in Germany, South Africa and Japan.

Fritz Haber: early years

Fritz Haber was born in Breslau (now Wroclaw, Poland) in 1868, son of a successful Jewish businessman in the dye industry. He grew up in the Kaiser's Germany, then undergoing enormous industrial expansion and national awareness, and boasting a superb scientific educational system. Briefly he worked in his father's business, then left to study organic chemistry in Berlin.

Further study followed at Zurich and Jena, and then at Technische Hochschule at Karlsruhe where Haber became professor of physical chemistry and over 17 years established his reputation through studies in thermodynamics and electrochemistry; he wrote *The thermodynamics of technical gas reactions* (1908) and developed an active research group.

Direct nitrogen fixation

At Karlsruhe, Haber studied the problem of direct ammonia synthesis that others had tackled. Wilhelm Ostwald made small amounts but the results were not encouraging; Le Chatelier attempted a direct synthesis but gave up following a laboratory explosion.

Initially Haber collaborated with Walther Nernst but he disputed Haber's calculations and doubted direct synthesis would be feasible technically. Haber checked his measurements and persisted. Direct synthesis is:

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad \Delta H = -92.4 \text{ kJ/mol}$$

Ammonia formation is both reversible and exothermic. Increasing temperature increases the reaction rate but at the expense of yield. Conversely, ammonia formation is favoured at lower temperatures but its formation is so slow as to be impractical.

Haber realised that high pressure would favour the reaction, as suggested by Le Chatelier's principle. The reaction was practical only through a compromise application of high temperature and pressure (Fig. 1), provided a suitable catalyst could be found to improve rates. Haber found conditions of about 500°C and 20 MPa (200 atm) produced a commercially viable yield of 10-20% liquid ammonia, using an osmium catalyst (or uranium) and recycling the feed gas.[5]

The Haber-Bosch process

Haber secured the patent for ammonia synthesis in 1909; however, further development needed industry support. Germany's synthetic dye manufacturer BASF bought Haber's patent, agreeing to pay him a *pfennig* for every kilogram of ammonia produced industrially; ultimately it made him a millionaire.[6]

The BASF engineer Karl Bosch[†] developed the process to full plant scale. He designed the high-pressure vessels and sourced hydrogen from water gas, while Alwin Mittasch developed the cheaper iron catalyst that required 20 000 tests to be done. It became the Haber-Bosch process.[3]

In 1913 BASF produced ammonia industrially at Oppau and a second plant near Leipzig in 1918. By 1929 world consumption of nitrogen had trebled, with more than 40% coming from direct fixation, about 20% from Chile saltpeter, 20% from coke-oven gas, 12% from cyanamide and only 1% from the arc process.[6]

Commercial production today uses modifications of Mittasch's original catalyst (magnetite, alumina and alkaline oxide additives) and recycles the feed gas. The major stages are:

- removal of sulfur from natural gas and reaction of clean methane with steam over nickel oxide catalyst

  $$CH_4 + H_2O \rightarrow CO + 3H_2;\ CO + H_2O \rightarrow CO_2 + H_2$$

- a secondary reforming, which occurs with air, to produce nitrogen

  $$2H_2 + O_2 + N_2 \rightarrow 2H_2O + N_2$$

- shift reactions, converting CO to CO_2 and providing additional hydrogen; this is done at variable temperature using mixtures of metallic catalysts

  $$CO + H_2O \rightarrow CO_2 + H_2$$

- removal of CO_2, leaving the required 1:3 stoichiometric ratio of N_2 and H_2, the synthesis gas.

Industrially ammonia is the source of fertilisers ammonium sulfate and, more importantly, ammonium nitrate, prepared entirely from air and water (hence, 'bread from air'). The high-pressure reaction with carbon dioxide yields urea via the carbamate intermediate (Bosch-Meiser process):

$$2NH_3 + CO_2 \rightarrow H_2NCO_2NH_4 \rightarrow (NH_2)_2CO + H_2O$$

The Haber-Bosch process remains a milestone, and opened up the entire field of high-pressure chemical engineering (e.g. coal hydrogenation, petroleum cracking, polyethylene production).

The Great War

When World War 1, the Great War, erupted in August 1914, Haber was already director of the Kaiser Wilhelm Institute for Physical Chemistry and Electrochemistry in Berlin. Dutifully he put the institute immediately at the service of the government and German industry; it investigated ways of conserving Germany's limited resources.

Explosives production requires a nitrate source such as Chilean saltpeter, but the Allied blockade cut availability to the German munitions industry at commencement of the war. Without nitrate Germany could not sustain the conflict beyond 1916.[7] The Haber process, however, made the blockade irrelevant and kept Germany fighting.

Using the Ostwald process (1902) ammonia converts almost quantitatively to nitric acid by burning in air in the presence of a platinum catalyst followed by hydrolysis of nitrogen oxides; thus:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$
$$2NO + O_2 \rightarrow 2NO_2 \rightarrow N_2O_4$$
$$2N_2O_4 + O_2 + 2H_2O \rightarrow 4HNO_3$$

Nitric acid leads to nitrate explosives; specifically, the manufacture of TNT (trinitrotoluene) from nitration of toluene available from coal distillation. The Haber process made Ostwald's route viable by providing ample ammonia feedstock.

Progressively, trench warfare produced a military stalemate, which Haber proposed could be broken by the use of a new form of warfare, poison gas. At Ypres in April 1915 chlorine gas was released successfully against French troops, causing thousands of casualties.

There was outrage at the new form of warfare. Haber's wife, Clara Immerwahr, was also a scientist, among the first women

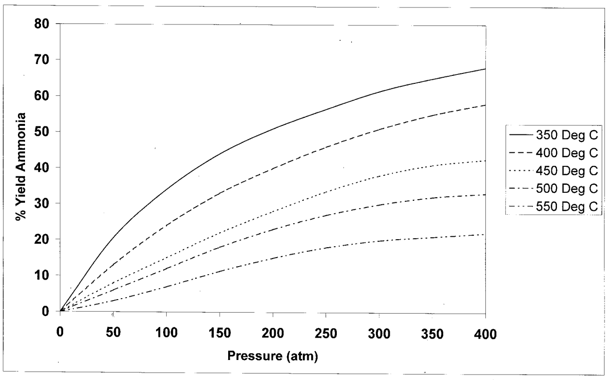

Figure 1. Percentage ammonia yield versus pressure with varying temperature.

in Germany awarded PhDs in chemistry. She objected violently to Haber's involvement, regarding it barbarous, 'an abomination of science'. One evening, following military testing of the gas, Clara took his service revolver and shot herself.[5,8]

Gas warfare continued. In France, Nobel laureate chemist Victor Grignard directed production of industrial quantities of phosgene (carbonyl chloride) and other gases. The Germans retaliated with mustard gas (dichloroethyl sulfide), a blistering agent; World War 1 became known as the 'war of the chemists'. However, chemical warfare did not produce the desired turning point in the war and Germany faced defeat.

Haber received the 1918 Nobel Prize for Chemistry for 'the synthesis of ammonia from its elements'. It was a controversial decision; some British and French scientists were vehemently opposed, believing he should be disqualified because of his chemical warfare activities.

Post-war years

Germany's defeat and the Treaty of Versailles ruined the country's economy. War reparations were crippling and repayment difficult because Germany's lucrative chemical patents were nullified. Haber felt personally responsible for his country's position, suggesting reparations could be paid from gold extracted from seawater.

For seven years he collected samples from various regions and secretly analysed it at his institute. Haber estimated that an average gold concentration of 0.008 ppm would make extraction viable, but the actual value was a thousand times lower and the project failed (1926).[5] Nevertheless the work provided the impetus for future recovery of bromine from seawater.[9]

Throughout the 1920s Haber continued to build the reputation of his institute, which became a prestigious centre for research in physical chemistry. He fostered relations with many foreign scientists, particularly from Japan.

The 1930s saw the rise of Nazism and the dismemberment of the great German university system; anti-semitic policy led to the dismissal of many academics. Despite his reputation and having years earlier converted to Christianity, Haber was threatened; even Max Planck intervened on his behalf, but Hitler was adamant that 'Jew Haber' should go.[5] He resigned (1933) and accepted an invitation from Cambridge University.

In early 1934 he left for Italy to escape the English winter, which badly affected his frail health. He suffered a heart attack and died in Basle, Switzerland.

Summary

Haber was a versatile chemist active in both academic and industrial environments, who said: 'It is not enough to seek and to know, we must also apply'. He made contributions to electrochemistry, thermodynamics, catalysis and combustion chemistry. Direct synthesis of ammonia is his lasting legacy; it remains a significant achievement of early 20th-century industrial chemistry that addressed a critical social issue. Gerhard Ertl received the 2007 Nobel Prize in Chemistry in part for elucidating the surface mechanism of ammonia synthesis on catalytic iron in the Haber process.

Haber's promotion of gas warfare is the other legacy, done in the spirit of a zealous patriot serving his country, but it damaged his and Germany's reputation, and gave impetus to the industrial-military complex. Perhaps his achievements remind us that science and technology are neither for us nor against us, but the choices we make in their application are.

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* Haber's rival in nitrogen fertilisers production, president of Bayrische Stickstoffwerke AG after World War 1.

† Received Nobel Prize in Chemistry (1931) with Friedrich Bergius for development of chemical high-pressure methods.

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