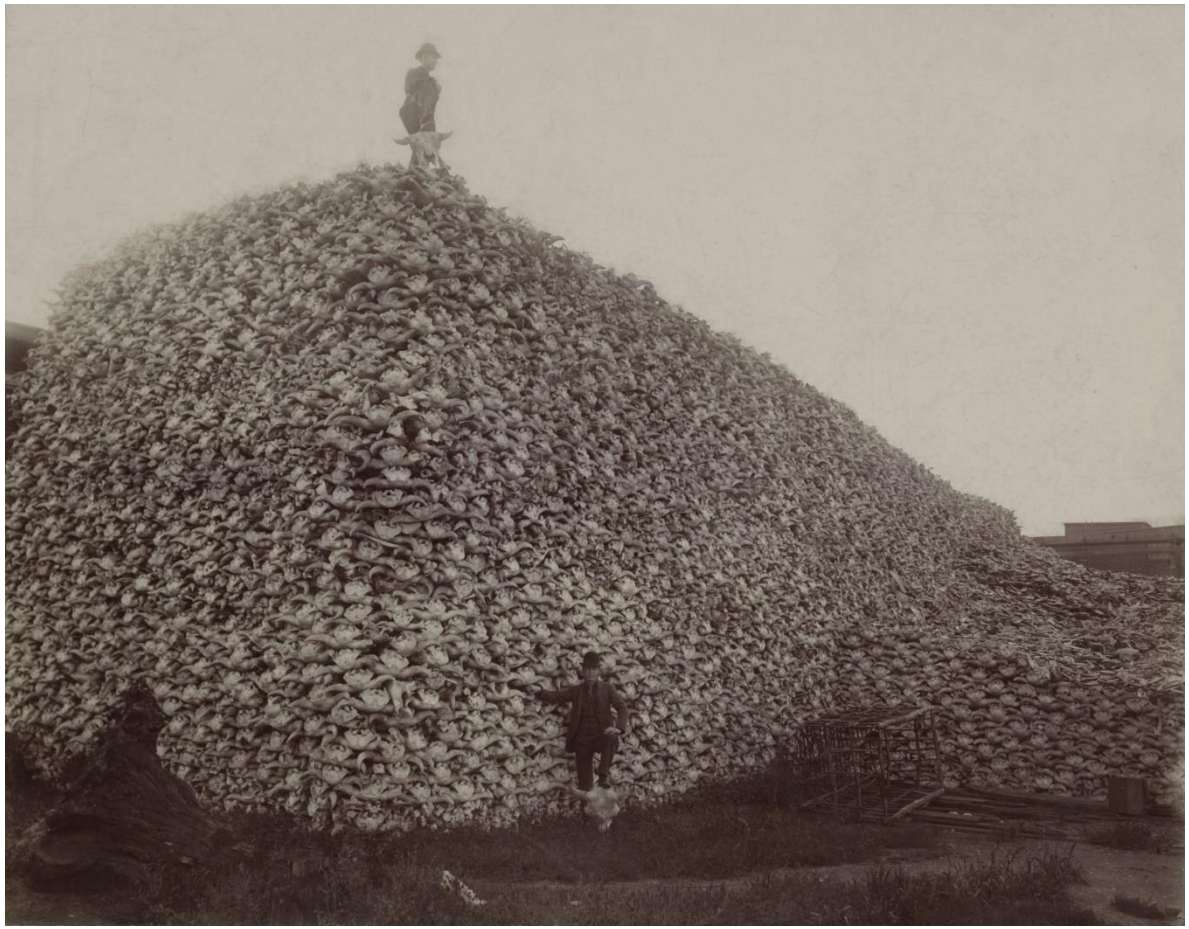
Haber Process (https://en.wikipedia.org/wiki/Haber_process)

- For several centuries, farmers knew that certain nutrients were essential for plant growth.
- In different parts of the world, farmers developed different methods of fertilizing the farmland.
- In China, human waste was scattered in rice fields.
- In nineteenth-century Europe, gangs of English graverobbers roamed the Continent, searching for skeletons to grind into fertilizer [citation needed].
- Justus von Liebig, German chemist and founder of industrial agriculture, claimed that England had "stolen" 3.5 million skeletons from Europe.

- In Paris, as many as one million tons of horse dung was collected annually to fertilize city gardens.
- Throughout the nineteenth century, bison bones from the American West were brought back to East Coast factories.



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- From the 1820s to the 1860s, the Chincha Islands of Peru were exploited for their high quality guano deposits, which they exported to the United States, France and the United Kingdom.
- The guano-boom increased economic activity in Peru considerably for a few decades until all 12.5 million tons of guano deposits were exhausted.
- Research was initiated to find alternative sources of fertilizer.

- The Atacama Desert, at that time part of Peru, was home to significant amounts of "Chilean saltpeter" (from sodium nitrate).
- At the time of the discovery of these deposits, the saltpeter had limited agricultural use.
- Then chemists successfully developed a process to turn the "Chilean saltpeter" into quality saltpeter to produce gunpowder.
- The saltpeter, could, in turn, be converted into nitric acid, the precursor of powerful explosives, such as nitroglycerine and dynamite.
- As exports from this region increased, tensions between Peru and its neighbors increased as well.

- In 1879, Bolivia, Chile, and Peru went to war over possession of Atacama Desert, the so-called "Saltpeter War".
- Bolivian forces were quickly defeated by the Chileans.
- In 1881, Chile defeated Peru and seized control of nitrate exploitation in the Atacama Desert.
- Consumption of Chilean saltpeter for agriculture quickly grew and Chileans standard of living rose significantly.
- Technological developments in Europe brought an end to these days.
- In the twentieth century, the minerals from this region "contribute minimally to global nitrogen supply."

- In the late nineteenth century, chemists, including William Crookes, President of the British Association for the Advancement of Science in 1898, predicted that the demand for nitrogen compounds, either in the form of fertilizer or explosives, would exceed supply in the near future.
- Following the work by Claude Louis Berthollet published in 1784, chemists knew ammonia to be a nitrogen compound.
- Early attempts to synthesize ammonia were performed in 1795 by Georg Friedrich Hildebrandt.
- Several others were made during the nineteenth century.
- In the 1870s, ammonia was an unwanted byproduct of making manufactured gas.

- Its importance emerged later, and in the 1900s the industry modified their facilities to produce it from coke.
- Still, production could not meet demand.
- For example, in 1910, production of fixed nitrogen from coke ovens totaled 230,000 tonnes, while Chile exported around 370,000 metric tonnes.
- In 1900, Chile, with its deposits of saltpeter, produced two-thirds of all fertilizer on the planet.
- However, these deposits rapidly diminished, the industry was dominated by an oligopoly and the cost of saltpeter rose constantly.
- To ensure food security for Europe's growing population, it was essential that a new economical and reliable method of obtaining ammonia be developed.

- Issues of food security were particularly acute in Germany.
- Its soil was poor and the country lacked an empire.
- A major consumer of Chilean saltpeter, Germany saltpeter imports totaled 350,000 tonnes in 1900.
- Twelve years later, it imported 900,000 tonnes.
- The Unitred States was in much better position due to the Guano Islands Act.
- In the years between 1890 and 1900, chemistry advanced on several fronts, and more scientists attempted to fix atmospheric nitrogen.
- In 1895, German chemists Adolf Frank and Nikodem Caro succeeded in reacting calcium carbide with dinitrogen to obtain calcium cyanamide, a chemical compound used as a fertilizer.

- Industrialization of the Frank-Caro process began in 1905. By 1918, there were 35 synthesis sites fixing 325,000 tonnes of nitrogen annually.
- However, the Cyanamide process consumed large amounts of electrical power and was more labor-intensive than the Haber process.
- Today, cyanamide is used primarily as a herbicide.
- Wilhelm Ostwald, considered one of the best German chemists of the early twentieth century, attempted to synthesize ammonia in 1900 using an invention.
- He interested BASF, who asked Carl Bosch, a recently hired chemist, to validate the device.
- After several tests, Bosch concluded the ammonia came from the device itself, not the atmosphere.

- In 1905, German chemist Fritz Haber published Thermodynamik technischer Gasreaktionen (The Thermodynamics of Technical Gas Reactions), a book more concerned about the industrial application of chemistry than to its theoretical study.
- In it, Haber inserted the results of his study of the equilibrium equation of ammonia:
- $N_2(g)+3\ H_2\ (g) = 2NH_3\ (g) - \Delta H$
- At 1000 °C in the presence of an iron catalyst, "small" amounts of ammonia were produced from dinitrogen and dihydrogen gas.
- These results discouraged his further pursuit in this direction.
- However, in 1907, spurred by a scientific rivalry between Haber and Walther Nernst, nitrogen fixation became Haber's first priority.

- A few years later, Haber used results published by Nernst on the chemical equilibrium of ammonia and his own familiarity with high pressure chemistry and the liquefaction of air, to develop a new nitrogen fixation process.
- He had no precise information on the parameters to impose on the system, but at the conclusion of his research, he was able to establish that an effective ammonia production system must:
  - operate at high pressure (on the order of 20 MPa[53]);
  - implement one or more catalysts[54] to accelerate the synthesis of ammonia;
  - operate at a high temperature (between 500 °C and 600 °C) to obtain the best efficiency in the presence of the catalyst;

- ❖ since about 5% of the $N_2(g)$ and $H_2(g)$ molecules react with each passage in the chemical reactor:
  - separate the ammonia from the other molecules by liquefaction, withdraw ammonia continuously,
  - inject again into the chemical reactor the $N_2(g)$ and $H_2(g)$ molecules that did not react;
  - recycle the heat produced.
- ❖ To overcome the problems associated with high pressure, Haber called upon the talents of Robert Le Rossignol, who designed the equipment necessary for the success of the process.
- ❖ Early in 1909, Haber discovered that osmium could serve as a catalyst. Later, he established that uranium could also act as a catalyst.

- Haber also obtained good results with iron, nickel, manganese and calcium.
- In the chemical equation shown above, the direct reaction is exothermic.
- This heat can be used to heat the reagents before they enter the chemical reactor.
- Haber's team developed a system that recycles the heat produced.
- In March 1909, Haber demonstrated to his laboratory colleagues that he had finally found a process capable of fixing atmospheric dinitrogen sufficient to consider its industrialization.
- On March 23, 1909, Haber informed BASF of his success, but August Bernthsen, director of research, could not believe that BASF wanted to engage in such a project.

- In fact, despite little chance of success, the company had already acquired the rights to the Haber process in 1908.
- According to Bernthsen, no industrial device was capable of withstanding, for a long period, such high pressure and temperature.
- In addition, the catalytic potential of osmium could disappear with use, which required its regular replacement despite the metal being scarce on Earth.
- However, Carl Engler, a chemist and university professor, wrote to BASF President Heinrich von Brunck to convince him to talk to Haber.
- Von Brunck, along with Bernthsen and Carl Bosch, went to Haber's laboratory to determine whether BASF should engage in industrialization of the process.

- When Bernthsen learned that he needed devices capable of supporting at least 100 atm (about 10 MPa), he exclaimed, "One hundred atmospheres!
- Just yesterday an autoclave at seven atmospheres exploded on us!
- Before deciding, Von Brunck asked for Bosch's advice.
- The latter had already worked in metallurgy, and his father had installed a mechanical workshop at home where the young Carl had learned to handle different tools.
- He had been working for several years on nitrogen fixation, without having obtained any significant results.
- He knew that processes that used electric arc furnaces, such as the Birkeland-Eyde process, required huge amounts of electricity, making them economically nonviable outside Norway.

- To continue to grow, BASF had to find a more economical method of fixing.
- Bosch said, "I think it can work. I know exactly what the steel industry can do. We should risk it."
- In July 1909, BASF employees came to check on Haber's success again: the laboratory equipment fixed the nitrogen from the air, in the form of liquid ammonia, at a rate of about 250 milliliters every two hours.
- BASF decided to industrialize the process, although it was associated with Norsk Hydro to operate the Schönherr process.
- Carl Bosch, future head of industrialization of the process, reported that the key factor that prompted BASF to embark on this path was the improvement of the efficiency caused by the catalyst.