The Nitrogen Industry.

By Prof. C. H. Desch.

THE discussion on the nitrogen industry, organised by Section B (Chemistry) of the British Association at the Hull meeting, proved to be a great success in spite of certain obvious difficulties in the way of such a discussion at the present time. There are many processes in the field for the fixation of nitrogen, and commercial rivalries make it impossible to secure completely frank and unbiassed accounts of the merits of the various systems. Much information of great scientific value has, for commercial reasons, to remain unpublished. The Section was therefore fortunate in obtaining a general survey of the subject from Dr. J. A. Harker, whose experience in this field during and since the war was exceptionally great, his practical acquaintance with most of the competing processes enabling him to take an impartial view of many controversial matters. His paper makes it easier for chemical readers to judge of the value of statements appearing in the technical periodicals and in the popular Press. According to Dr. Harker, there is little to be added in the way of statistical material to the Report of the Nitrogen Products Committee published some eighteen months ago, while the fluctuations in the German exchange make it quite unprofitable to discuss German conditions of production or the possibility of dumping, topics which would otherwise have been attractive to the author of such a paper. The nitrogen question has attracted so much public attention that it has even found its way into school examination papers, although profound ignorance on the subject prevailed five or six years ago, not only among the general public, but also in the circle of high officials directly concerned with questions of national importance.

The oldest process for the synthesis of nitrogen compounds from atmospheric nitrogen is that which employs the electric arc. The great plants in Norway, of immense size and working with the greatest success, are avowedly derived from the laboratory apparatus of the late Lord Rayleigh, and Prof. Birkeland stated that his decision to establish the process as an industrial one was based on the famous presidential address to the British Association by Sir William Crookes. Lord Rayleigh's experiments included the measurement of the relation between the energy consumed and the nitrogen fixed, and it is a striking fact that even now less than two per cent. of the energy of the average arc furnace is absorbed as chemical energy in the initial oxidation of the nitrogen. The modern plants are of enormous size, the two plants at Rjukan, for example, employing a total of 200,000 kilowatts, generated at an astonishingly low cost by means of water power. Several modified arc processes have been tried experimentally, including the Kilburn Scott three-electrode furnace. The use of enriched air has been tried on a large scale by a company having works in Switzerland and Germany, a closed circuit being used, and the nitrogen peroxide removed by cooling instead of absorption. This operation is not free from danger, and serious explosions have taken place. The arc furnace plants erected in France during the war have been closed, the power plants being required for their original purpose, the electrification of railways.

Of the many processes for the production of synthetic ammonia, the original Haber process, the most familiar of all, has been successfully worked by the Badische Co. at Oppau, and at the even larger works recently completed at Merseburg in Saxony. The pressure in this process is 200 atmospheres, which is not now regarded as high, and the gases move slowly through reaction vessels 40 feet long and 3 feet in external diameter, the walls being 6 inches thick. The gases are pre-heated and circulated. The process worked out at University College, London, by the Nitrogen Products Committee uses higher gas velocities, and was planned to yield about 5 kgm. of ammonia per hour for each litre of space filled with catalyst, instead of 400 gm. as in the Haber system. The first American plant at Sheffield, Alabama, used activated sodamide as the catalyst, but it is not surprising, in view of the action of water vapour on this substance, that it proved a failure; the later modified plant of the Solvay Process Co., now making liquid ammonia for the refrigerating industry, has avoided the defects.

The Claude process uses very high pressures of 900-1000 atmospheres, and the issuing stream contains as much as 25 per cent. of ammonia. Circulation is replaced by multiple stage working, and the reaction vessels, made by a Sheffield steel firm from a special heat-resisting material, are surprisingly small. Hydrogen is to be produced by an improved process from coke oven gas. Electrolytic hydrogen is used on several plants, notably at Terni in Italy, and it seems likely that where water power is cheap, hydrogen can be economically prepared by this means, provided that the form of the cell can be improved.

Cyanamide, regarded by some as obsolete, remains the cheapest form of combined nitrogen, but in spite of this, many of the war works using this process have been closed. The largest plant is that of the American government at Mussel Shoals, the future of which is still uncertain. The German cyanamide plants are being increased in size. A disadvantage of this compound for agricultural purposes is that it is liable to change into dicyandiamide, but attempts are being made to convert it into other more valuable compounds. One American company is converting it into a mixed fertiliser, ammonium phosphate, which is useful but at present too costly. In Switzerland the calcium cyanamide has been converted to free cyanamide by carbonic acid, and then into urea. Mixed with monocalcium phosphate, a product known as phosphazote is obtained, and this substance is used for vines, the cost not being high. Mixed salts containing ammonium nitrate have suffered in popularity through the Oppau explosion, but the use of powerful blasting cartridges, which caused that explosion, is indefensible.

The cyanide process, the oldest of all nitrogen fixation processes, is in use in America for making the acid for plant fumigation, and researches are in progress with the object of cheapening the manufacture.

In concluding his paper, Dr. Harker directed attention to the large increase in the German capacity to produce synthetic nitrogen compounds, and the erection of new plants in that country. At the end of this year Germany will be independent of all importation of nitrates, while the large munition works in this country are being dismantled. The subject, therefore, has political importance as well as scientific and commercial interest.

Mr. J. H. West's paper dealt with the manufacture of the nitrogen and hydrogen required for synthetic ammonia processes. Three volumes of hydrogen being required for one of nitrogen, and the former being the more expensive gas, the cost of the process depends mainly on that of the hydrogen. The electrolytic process is convenient, and yields pure hydrogen, but the capital cost of the plant is high, and the method is only practicable where cheap hydro-electric power is available. Coke oven gas may be used, the method employed being that of liquefying all the gases present except hydrogen, but in this case the small quantity of carbon monoxide which always remains mixed with it must be removed by chemical washing or by conversion into methane, the gas being a poison to the catalyst in the subsequent ammonia synthesis. Water gas may be used, a reaction with steam being brought about in presence of a catalyst: $CO + H_2O = CO_2 + H_2$. In a modified process, due to the author and A. Jacques, the coal is treated by a process of complete gasification, and the gaseous products treated in the same apparatus to yield carbon dioxide and hydrogen with a catalyst. Nitrogen is made by the liquid air process, or by mixing air and hydrogen in such proportions that on passing over a suitable catalyst the oxygen is converted to water, and a mixture of nitrogen and hydrogen in the required proportions remains. In the Haber process, water gas and producer gas are mixed in such proportions that a correct mixture is left after removal of the carbon monoxide.

Both this paper, and the succeeding one by Mr. C. J. Goodwin, were presented in the absence of their authors, so that they suffered in the discussion. Mr. Goodwin described the Häusser process for the production of nitric acid by exploding nitrogen and oxygen with a fuel gas in a bomb. Although the plant has hitherto been on an experimental scale, it is expected that the new bombs of 1200-1500 litres capacity will give commercial yields, and the use of stainless steel has overcome much of the corrosion difficulty. The absorption towers have been greatly reduced in size by employing nickel-chromium steel or silicon-iron for the vessels, under a pressure of 2·5-4 atmospheres. The suggestion has been made that a special gas engine or Humphrey pump might be used in place of a bomb, in order to utilise the heat energy of the fuel more economically, but it remains to be seen whether such a change would prove advantageous on the whole. The main advantage of the process is its compactness, the size of the plant being small, especially when gases of high calorific value are used.

Dr. E. B. Maxted's contribution concerned the question whether nitrogen fixation, based on water power, could be economically undertaken in this country. Under present conditions, there are several sites in these islands where it should be possible to produce hydro-electric energy for *4l.*-*5l.* per kilowatt-year, the greater part of this sum representing interest on the capital cost. This would allow of the production of electrolytic hydrogen at a cost of *1s. 7d.* per 1000 cubic feet, which does not compare unfavourably with the cost of hydrogen from fuel. Greater economy would be effected if uses for large supplies of oxygen in the chemical industries could be found. Comparing together the ammonia and cyanamide processes, it appears that a given amount of power, say 10,000 kilowatts, being available, either process would result in the fixation of about the same quantity of nitrogen, but the ammonia process would yield large quantities of oxygen as a by-product, while the cyanamide process would require the bringing of anthracite and lime to the site. There would be some compensating conditions, such as the greater simplicity of the cyanamide process, and the necessity of fixing ammonia by means of an acid.

Mr. E. Kilburn Scott denied the contention that the arc process is uneconomical. It has been stated that in Norway nitric acid could be made profitably where electric energy costs *10l.* per kilowatt-year, while the Scottish schemes can provide the same quantity for *4l.* The arc process is the only one capable of utilising off-peak power, and where large generating stations are set up it is quite economical. Moreover, calcium nitrate is the best of all artificial fertilisers. Little else emerged in the discussion. It is clear that processes which promised well during the exceptional conditions of the war have to be re-examined very carefully in regard to their practicability under ordinary conditions of competition, and it has yet to be demonstrated that synthetic processes can be established successfully where power has to be obtained from the combustion of coal. Whatever may prove to be the future of these processes, Dr. Harker's review of the present position of the question will be of value, as an addition to the important memoirs already published from official sources.

The Thermal Basis of Gas Supply.

By Prof. John W. Cobb.

The amount of attention which has been given in the Press during the past few months to the new basis of charge for gas introduced by the Gas Regulation Act of 1920, is at first sight somewhat surprising and unexpected. To the scientific mind there seems to be so little in it that calls for mental strain in its comprehension, or for criticism in its introduction.

Gas is now to be sold at so much per therm, and the therm is simply 100,000 British Thermal Units—*i.e.* a convenient multiple of what is the most widely known and generally accepted unit of heat. A