

ON THE OXIDATION OF ATMOSPHERIC NITROGEN IN ELECTRIC ARCS.

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PROFESSOR S. P. THOMPSON, F.R.S., *in the Chair.*)

Last year, in the month of May, a factory was started at Notodden, in Norway, for the manufacture of calcium nitrate from air and limestone by the aid of electric flames (see Figs. 1 and 1a).

Thanks to the rapid progress made by electrotechnics, it has thus already become possible to evolve from the famous old discovery of the chemical combination of nitrogen and oxygen in an electric spark, a technical method for the production of saltpetre.

The nitrate problem, as we know, has gained, within a short space of time, a very important place among technical problems, a fact which is due to the enormous consumption of Chili saltpetre.

During the last twenty years more than four times as much saltpetre has been exported from Chili as during the preceding twenty years; and the requirements of the world still seem to be increasing—during the last ten years at an average rate of about 4 per cent. per annum.

At the present time about 1·5 million tons are annually exported from Chili; but experts declare that exportation such as this will empty the Chilean mines by the year 1940 at the latest.

In 1898 Sir William Crookes, in his address as President of the British Association, drew the attention of the entire civilised world to the question of food-supply. There was a note of warning in his statement that the population of the world is increasing so rapidly that the supply of wheat will shortly not be sufficient to feed it. He further prepared us for the approaching exhaustion of the world's stock of fixed nitrogen, the great fertiliser for wheat, used in ever-increasing quantities.

Among his statistics are the following* :—

“The present acreage devoted to the world's growth of wheat is about 163,000,000 acres. At the average of 12·7 bushels per acre, this gives 2,070,000,000 bushels. But thirty years hence the demand will be 3,260,000,000 bushels, and there will be difficulty in finding the necessary acreage on which to grow the additional amount required. By increasing the present yield per acre from 12·7 to 20 bushels, we should, with our present acreage, secure a crop of the requisite amount. Now from 12·7 to 20 bushels per acre is a moderate increase of productiveness, and there is no doubt that a dressing with nitrate of soda will give this increase and more.

“The action of nitrate of soda in improving the yield of wheat has been studied practically by Sir John Lawes and Sir Henry Gilbert on their experimental field at Rothamsted. This field was sown with wheat for thirteen consecutive years without manure, and yielded an average of

* *Nature*, No. 1,506, vol. 58, 1898.

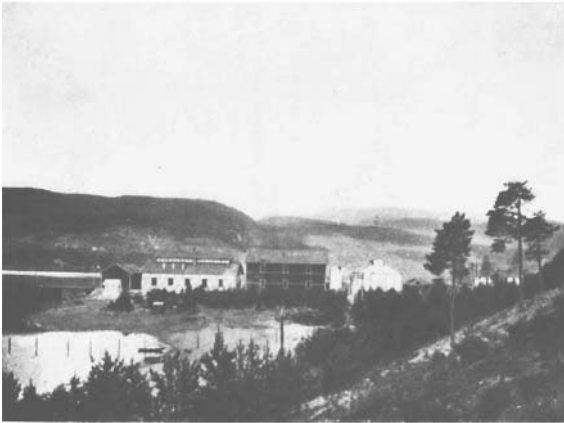


FIG. 1.

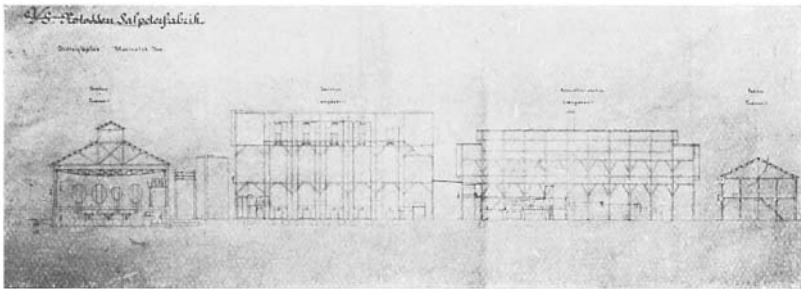


FIG. 1a.

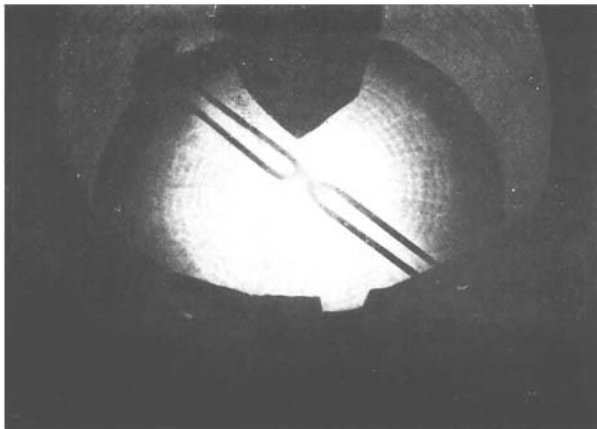


FIG. 3.

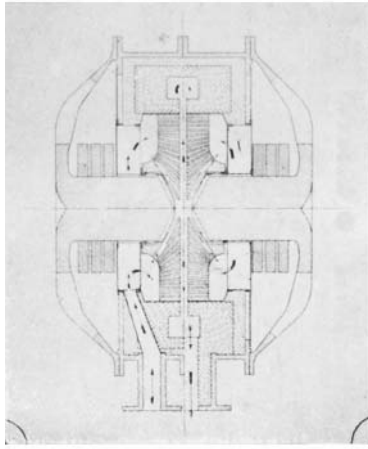


FIG. 6.

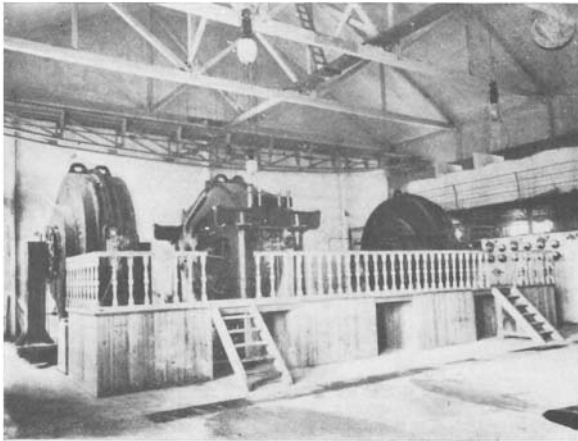


FIG. 7.

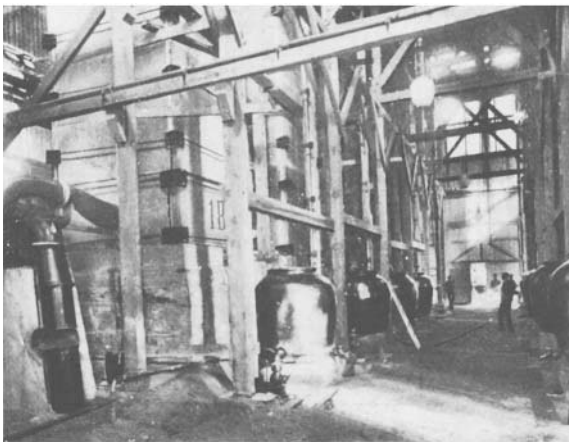


FIG. 8.

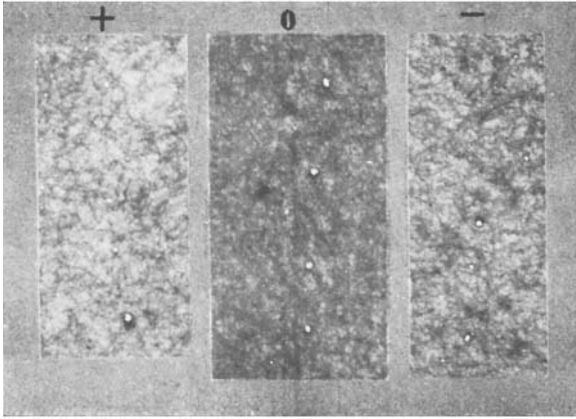


FIG. 9.

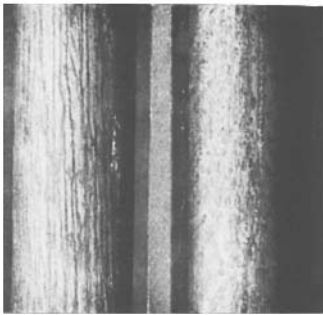


FIG. 10.

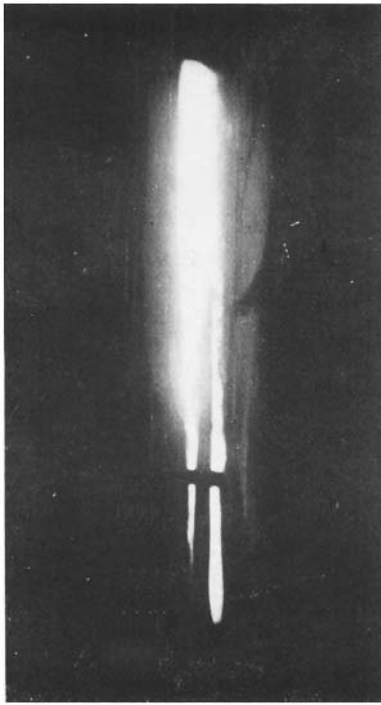


FIG. 11.

ATMOSPHERIC NITROGEN IN ELECTRIC ARCS 99

11·9 bushels to the acre. For the next thirteen years it was sown with wheat, and dressed with 5 cwt. of nitrate of soda per acre, other mineral constituents also being present. The average yield for these years was 36·4 bushels per acre—an increase of 24·5 bushels.

“At this rate, to increase the world's crop of wheat by 7·3 bushels, about 1½ cwt. of nitrate of soda must annually be applied to each acre. The amount required to raise the world's crop on 163,000,000 acres from the present supply of 2,070,000,000 bushels to the required 3,260,000,000 bushels, will be 12,000,000 tons distributed in varying amounts over the wheat-growing countries of the world.

“If we assume a liberal estimate for nitrate obtained from the lower-grade deposit, and say that it will equal in quantity that from the richer quality, the supply may last, possibly, fifty years, at the rate of a million tons a year; but at the rate required to augment the world's supply of wheat to the point demanded thirty years hence, it will not last more than four years.”

In connection with these statements by Crookes, it is interesting to hear what M. Grandeau, in a paper just published,* brought forward from French statistics. †

The crops harvested upon the cultivated area of France abstract annually 600,000 tons of nitrogen—in round numbers—from the soil. It is proved that the nitrogen returned in stable manure—even supposing it were all taken to the fields, which is not the case—would not represent more than 327,000 tons.

Now France consumes only 230,000 tons of Chili saltpetre per annum, which represents 31,200 tons of nitrogen, while the deficiency is 273,000 tons. The amount imported is thus only 11 per cent. of the deficiency produced by the removal of the crops.

Chili nitrate is a first-rate fertiliser. One hundred kilogrammes of nitrate give, on an average, the following mean excess of products:—

Cereals	300 to 400 kilogrammes of grain, and straw to correspond.
Potatoes	35 metric quintals.
Beetroot	55 metric quintals.
Roots, Indian corn	45 to 55 metric quintals.

The remarks cited above will make clear to every one the great importance of the nitrogen problem. And now that this problem has been solved, as I shall presently show, and the atmosphere itself freely offers us the raw material, so that out of the air over each square mile of the earth's surface we can make more saltpetre than is to be found in all Chili, we have no longer any reason to fear “the near exhaustion of the world's stock of fixed nitrogen.”

Neither have we any reason to fear that air will not be freely offered to us for this purpose, for even peasants from some of the most beautiful parts of Norway have written to me and asked if I would not make use of the air from their own parts of the country, which, as they say, “is of such exceedingly fine quality.”

The nitrogen problem has been solved in two ways.

By taking as his starting-point the power possessed by several metals of directly-fixing nitrogen, Professor Frank, of Berlin, in collaboration with Mr. Caro, has been led to the discovery of his beautiful method, namely, the introduction of calcium carbide as an absorbent of pure nitrogen.

* L. Grandeau: *La production électrique de l'acide nitrique avec les éléments de l'air*. Paris, 1906.

† E. Tisserand: *Etude sur l'économie rurale de la France. Statistique décennale de 1882*.

At a red heat, the carbides of the metals of alkaline earths absorb the nitrogen supplied to them, and are thereby transformed into metallic salts of cyanamide. These salts are capable of many kinds of chemical changes. After being for a short time in the soil, for instance, they decompose and form ammonia. Calcium cyanamide can therefore be employed directly as a fertiliser, and is manufactured for this purpose by the Cyanidgesellschaft in Berlin, whence it appears upon the market under the name of lime-nitrogen.

The other way in which the nitrogen of the atmosphere can be fixed very simply and to great advantage is by the oxidation of nitrogen in electric arcs.

This method has been followed by a great number of scientists and inventors, whose endeavours have been chiefly directed towards the discovery of a stable and practical form of electric arc that could serve as a flame for the oxidising of nitrogen. A flame such as this, burning with a power of up to 1,000 kilowatts, and fulfilling every requirement as regards reliability for manufacture on a large scale, has been used for the first time in the "Birkeland-Eyde Process," the method now employed in the Notodden Saltpetre Manufactory, and also to be employed at the new Svælgfos-Notodden Works of about 30,000 H.P., which will be completed next year.

The aim of the Paper which, by the invitation of your Council, I have now the honour of laying before this Society, is to review the progress recently made with regard to the oxidation of atmospheric nitrogen, and to indicate its possible future advances, paying, as is natural, special attention to the above-mentioned Birkeland-Eyde Process.

ELECTRIC FLAMES FOR OXIDISING NITROGEN.

In 1892 Crookes exhibited at one of the soirées of the Royal Society an experiment on the "Flame of Burning Nitrogen," in which, by passing a strong induction current between terminals, the air burned with a flame producing nitrous and nitric acids.

Before him, as you are aware, Priestley and Cavendish, about the year 1780, oxidised atmospheric nitrogen in small quantities by electricity* ; and in 1880 Spottiswoode and Dewar produced and studied electric flames in air.

In 1897 Lord Rayleigh published his "Observations on the Oxidation of Nitrogen Gas." † These observations were made in the course of the famous experiments that led him, in collaboration with Sir William Ramsay, to the discovery of argon. In a glass vessel of fifty litres' capacity, he had burning an electric flame, representing rather more than 1 H.P. With this apparatus

* In the Preface of the *History of Electricity*, Fourth Edition, 1775, p. xxiv., Priestley says :—"Also, in my *Observations on Different Kinds of Air*, the reader will find that I have demonstrated that the electric matter is, or contains, phlogiston, by showing that it affects all kinds of air as phlogiston does ; particularly diminishing common air one-fourth and making it noxious, so as to make no effervescence with nitrous air." In the Edition of 1790 of *Observations on Different Kinds of Air*, Priestley again describes the effect of the electric spark on air. Here he says (Part II, p. 250) : "But Mr. Cavendish has proved that nitrous acid was formed in this process by an union of the dephlogisticated and phlogisticated air in common air."

In the memoir, "Experiments on Air," by Cavendish (*Phil. Trans.*, vol. 75, 1785), Cavendish says : "When the electric spark was made to pass through common air, included between short columns of a solution of litmus, the solution acquired a red colour, and the air was diminished, centormably to what was observed by Dr. Priestley."

† *Journ. of the Chem. Soc.*, 71 (1897).

he was able to absorb about 20 litres per hour of a mixed gas consisting of about 11 parts of oxygen to 9 of air. This was done by absorbing the oxides of nitrogen formed by causing a fountain of caustic-soda solution to play upon the top of the flask containing the arc, this serving the double purpose of keeping the vessel cool, and of presenting a large absorbing surface to the gases produced by the arc. The result deduced from his figures is that one kilowatt-hour would be required to form 50 grammes of nitric acid.

It was in this Paper by Lord Rayleigh that mention was first made of the electrical difficulties met with in producing a steady high-tension flame for oxidising nitrogen. The electric conditions in the flame are unstable; it is necessary to introduce great ballast-resistance, thus making the factor of reduction of the electrical machinery very unfavourable.

The transformer used in Rayleigh's experiments had an open secondary a voltage of nearly 8,000; but this fell to 2,000 or less when the discharge was running.

The reason why a given constant tension cannot be employed directly is probably to be found in the fact that the electric conductivity of the heated air increases rapidly with the temperature.

The conditions here touched upon are of such essential importance to wholesale production, that, as regards the nitrogen oxidising flame, the quality of burning steadily, with a good factor of reduction, is second in importance only to that of giving the largest possible output.

Although Rayleigh's apparatus can scarcely be made adaptable to technical uses, he was, at any rate, the first to show that with electric arcs it is almost possible to fix nitrogen in an economical manner, in proportion to the electric energy expended. The solution of the problem of producing assimilative nitrogen, *e.g.*, saltpetre, from air, after his experiments, followed in the natural order of things, so to speak.

At the beginning of the twentieth century a whole series of experiments was indeed made, which found expression, partly in scientific attempts to lay down conditions for the attainment of the most advantageous output, partly in patenting methods, and partly in taking direct steps towards a wholesale, synthetic production of saltpetre from air.

Among such experimenters we will mention Naville and Guye* in Geneva, McDougall and Howles† in Manchester, Kowalski and Moscicki‡ in Freiburg, Bradley and Lovejoy|| in the United States, and Muthmann and Hofer§ in Munich.

These attempts, which are already well known, and, in accordance with the aim of this Paper, will not be discussed in detail here, were not altogether encouraging as regards the question of the possibility of the technical working out of the nitrogen problem.

Among the above-named men, Bradley and Lovcjoy, and Kowalski and Moscicki have brought into use mainly new forms of electric flames, adapted to the oxidation of atmospheric nitrogen.

The first of these employed a continuous current at a potential of 10,000 volts. Owing to the difficulty of keeping discharges at voltages such as these in steady operation, they employed a slowly rotating framework with

* *D.-R.-P. Nr.* 88,320 (1895).

† *Manchester Memoires*, 44 (1900).

‡ *Société Internationale des Electriciens*, 2 Serie, tome iii. (1904).

|| *Electrochem. Industry*, I (1903).

§ *Chem. Ber.* 36 (1903).

projecting electrodes, which, on approaching other projecting platinum rods in the course of their revolution, provoked discharges which were again immediately interrupted.

The fundamental idea running all through their experiments is the necessity of obtaining electric arcs of the greatest possible length and smallest possible transverse section, in order that the greatest possible volume of air might be brought into contact with the surface of the arc. Bradley and Lovejoy therefore divided up an arc of great energy into a countless number of small arcs; in this way they used as much as 414,000 arcs per minute in an apparatus of only a few kilowatts. It will be easily understood that a method such as this must have been accompanied by considerable technical difficulties, and it soon proved that their process was not a commercial success, although they obtained a considerable amount of nitric acid per kilowatt-year.

Among the advantages and defects of Bradley and Lovejoy's arrangement for the oxidation of nitrogen, the following may be noted:—

It is certainly wise to evade the difficulties connected with the unstable electrical conditions in a powerful arc by distributing the electric energy over a large number of variable arcs of short duration. In the average, the energy consumed in the arcs can then be kept fairly constant without the necessity of employing great inductive resistance. But in concluding from the results of their experiments that it was necessary, for the sake of the output, to distribute the electric energy over a multitude of exceedingly *small* arcs, the experimenters have certainly come to a wrong conclusion.

With regard to MM. Kowalski and Moscicki's method, these experimenters, having observed that the output of NO with a large number of periods is better than with the usual number of periods from ordinary alternators, oxidised nitrogen in high-tension flames of up to 50,000 volts with oscillating currents of from 6,000 to 10,000 periods per second.

The increase in the output, occasioned by the greater frequency of the current, as stated by Kowalski and Moscicki, is not produced in all forms of electric nitrogen-flames; for the author has made comparative experiments with machines of 50 periods and 100 periods per second, and has not been able to detect any difference in the output in flames of the kind employed in the Birkeland-Eyde process.

MM. Kowalski and Moscicki are still continuing their attempts at this method, where they have to master the difficulties connected with the high voltage employed.

We will now pass on to the peculiar form of high-tension flame which constitutes the principal element in the Birkeland-Eyde process for the fixation of atmospheric nitrogen, as adopted in the nitrate manufactories at Notodden.

This flame, which has never before been employed in technics, has already proved to be a powerful technical aid in producing various chemical reactions, and is, therefore, deserving of a detailed description.

When two pointed copper electrodes, attached to a high-tension alternator, are placed equatorially between the poles of a powerful electromagnet, in such a way that the terminals of the electrodes are in the middle of the magnetic field, an electric disc-flame will be formed such as is shown diagrammatically in Fig. 2, and as photographed in Fig. 3. The photographed flame, which represented about 250 H.P., was established between water-cooled electrodes made of copper tubing of 15 mm. diameter.

The working potential employed for this is 5,000 volts, the current is an alternating current of 50 periods per second, and the terminals of the

electrodes are at a fixed distance of about 8 mm. from one another. Even with flames of 750 kilowatts at 5,000 volts, the same kind of electrodes can be employed; and here, too, the distance between the terminals of the electrodes is not more than about 1 cm. By the cooling of the electrodes with water, about 75 per cent. of the electric energy engaged between the electrodes is removed by the water as heat.

The formation of these disc-flames may be explained in the following manner: At the terminals of the closely adjacent electrodes, a short arc is formed, thus establishing an easily movable and ductile current-conductor in a strong and extensive magnetic field, *i.e.*, from 4,000 to 5,000 lines of force per square centimetre in the centre. The arc is thus formed then moves in a direction perpendicular to the lines of force, at first with an enormous velocity, which subsequently diminishes; and the extremities of the arc retire from the terminals of the electrodes. While the length of the arc increases, its electric resistance also increases, so that the tension is heightened until it becomes sufficient to create a new arc at the points

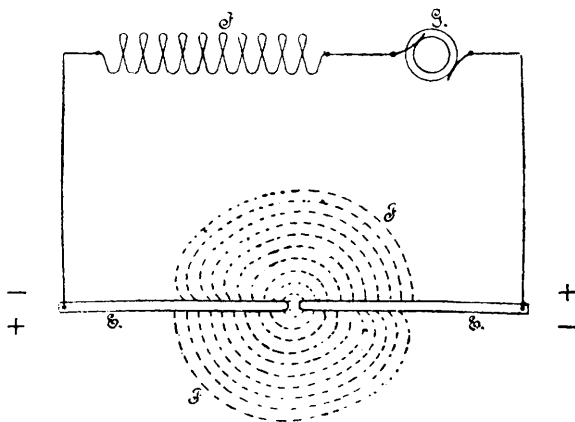


FIG. 2.

of the electrodes. The resistance of this short arc is very small, and the tension of the electrodes therefore sinks suddenly, with the consequence that the outer, long arc is extinguished. It is assumed that while this is taking place, the strength of the current is regulated by an inductive resistance in series with the flame.

In an alternating current (see Fig. 2), all the arcs with a positive direction of current run one way, while all with a negative direction run the opposite way, presupposing the magnetising being effected by direct currents. In this way, a complete, luminous, circular disc is presented to the eye.

The flame extends farther along the *positive* electrode than along the negative.

The extremities of an arc may sometimes appear like glowing spots upon the backs of the electrode. The spots of light on the positive electrode are small, and lie exceedingly close to one another; while those on the negative electrode are larger, and the distance between them is greater. The reason of the appearance of these spots of light is that the arcs, so to speak, melt or solder themselves to the electrodes, so that the magnetic force can only make the extremities of the arcs move along the electrodes in tiny leaps. It is

evident from the curvature of the arcs that they cling more closely to the negative than to the positive electrode ; and, therefore, the flame extends farther along the positive electrode than along the negative.

When the flame is burning it emits a loud noise, from which alone an impression may be obtained of the number of arcs formed per second in the flame. If the matter is to be more minutely investigated, this may be done by the aid of an oscillograph, by means of which the tension-curve for the electrodes, and the current-curve, can easily be drawn.

Figure 4a shows the tension-curves for the electrodes ; with the disc-flame in operation the jagged curve is obtained, while the comparatively regular sine curve gives the tension-curve when the electrodes are screwed so far from one another that the flame is extinguished.

It will be seen that in this case several arcs are formed in the flame at each reversal of the current, and, therefore, altogether, several hundred arcs per second, as the alternating current employed had 50 periods per second. This occurs when the magnetisation is too high, or the distance between the electrodes too small ; for, as a rule, with large, steadily-burning



FIG. 4a.

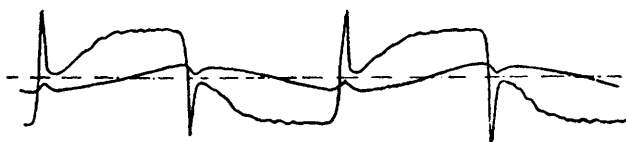


FIG. 4b.

flames, only one arc is formed at each reversal of the current, as shown in Fig. 4b.

Here the curve with the sharp points is the tension-curve, the other being the current-curve. Unfortunately these curves were not taken simultaneously, but one after the other, as the oscillograph employed was not a duplex one. It will soon be altered, however, so that current and tension curves can be taken simultaneously ; and careful investigations will then be made, in order to throw light upon various questions of theoretic interest. The current and tension curves we have already taken show, moreover, that the electric conditions in the flame may change very considerably with the relative proportions of the working current and the magnetic field.

Before passing on to consider the technical arrangements that have been made for the manufacture of saltpetre, we will briefly mention a newly patented arrangement for an electric arc for oxidising nitrogen.* The patent is taken out by the firm of Badische Anilin & Soda Fabrik, at whose head are men who, as experimenters also, are second to none. Within the last few weeks, the sad news has been received of the death of one of these, the celebrated Dr. Rudolf Knietsch.

* French Patent No. 357,358.

The flame in question is a single arc, drawn out to a length of several metres in a long vertical tube, through which air is blown, while at the same time a certain whirling motion is imparted to it. Little is known about the experiments made by the patentees with this very interesting flame, so that it is too early to express any opinion as to their process. At our trial works at Arendal, we have, of course, made experiments on a large scale with this arrangement in order to compare it with our own, but we naturally have no right to say anything on the subject.

ELECTROTECHNICAL PROCESSES FOR THE MANUFACTURE OF SALTPETRE.

The first to attempt a wholesale, synthetic production of nitric acid from air, were, as we know, Messrs. Bradley and Lovejoy, who formed a Company with a considerable capital for that purpose, called the Atmospheric Products Company, and built a small trial factory at the Niagara Falls. The electrical apparatus employed there has already been briefly described; it was rather complicated, and not sufficiently stable, so that both the cost of erection and maintenance per kilowatt were disproportionately large. The great expectations that had been raised for a time by this American undertaking were doomed to disappointment, as the Company ceased operations in the summer of 1904.

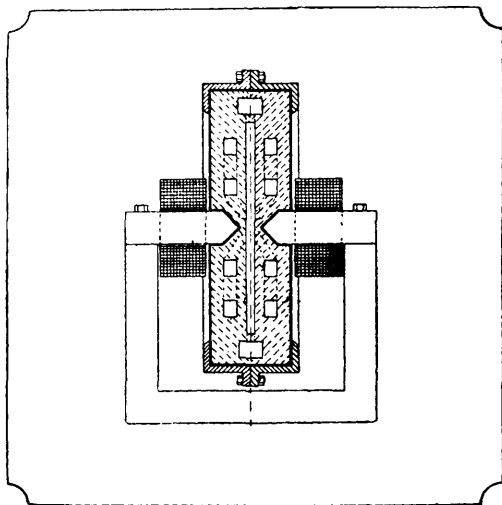


FIG. 5.

Nor do MM. Kowalski and Moscicki seem to have been quite successful, at least, up to the present date. Their previously-mentioned electric arrangement, with alternating currents with a tension of up to 50,000 volts, has, however, been brought into use in some experimental works at Freiburg.

While thus the attempts begun before 1903 did not result in any method for a wholesale production of saltpetre that could take its place in practical life as a commercial method, Eyde and the author, in combination with the Norwegian Nitrogen Company, were able in 1904 to display results that immediately convinced the experts that had been called in that the saltpetre problem had now been solved in a satisfactory manner; for we succeeded, with simple and easily-regulated apparatus, in working with so large an

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amount of energy, that the quantity of nitric acid produced was, for the first time, sufficiently large to justify a direct transfer of results and calculations to industrial undertakings.

The alternating-current disc-flame already mentioned was enclosed in a special furnace, which was lined with fire-brick, and furnished with a metal casing. Figs. 5 and 6 show two such furnaces, one of an older, the other of a newer type. The fire-chamber of the furnace is narrow, in the direction of the lines of force—from 5 to 15 cm. wide—made partly of perforated chamotte air being conveyed to the disc-flame, in an evenly-distributed supply, through its walls. The system of magnets is composed of two powerful electromagnets, their extremities turned in towards the fire-chamber. The magnetic circuit is closed either as in a horse-shoe magnet, or through the shield-like, cast-steel casing of the furnace. The air is driven into the central region on both sides of the flame by gentle pressure from a Root's blower; and after passing in a radial direction arrives at a peripheral channel, whence it is conducted away. The horizontal electrodes are made of copper tubing, 15 mm. in diameter; whose terminals are within about 1 cm. of one another, and are cooled by water in circulation, which keeps them from fusing. The electrodes are exchanged and repaired after being in use for about three hundred hours, the exchange itself taking about fifteen minutes to accomplish.

At the Notodden Saltpetre Manufactory there are three such furnaces (see Fig. 7) in constant activity, each employing 500 kilowatts. These furnaces burn with an astonishing degree of steadiness, with a variation in energy of only 2 or 3 per cent., although the electrodes have no automatic regulation. It often happens that the assistant who attends to the furnaces does not need to touch any of them all through his watch; and it has happened that a furnace has burned for forty hours without being attended to. The furnaces themselves give notice of anything going wrong, for the flame then begins to roar; and the warning comes in ample time to allow of an adjustment before the flame is extinguished. The furnaces work with a factor of reduction of 0·7. With a working potential of 5,000 volts, 3,500 volts and more are obtained on the electrodes.

As already mentioned, the furnaces are lined with fire-brick. Even the large, inner surfaces of the furnace have shown that they remain very stable, the reason of this evidently being that, in spite of the enormously high temperature of the disc-flame, the temperature on the walls does not rise above 700° C. during normal working, owing to the cooling effect of the current of air.

We have estimated that two or three fire-brick linings would be required per annum for each furnace; but this will certainly prove to be too high an estimate on the average, and the fire-brick linings will last longer than they are assumed to do. In the new saltpetre manufactory at Notodden, which is to obtain about 30,000 H.P. from Svælgfos, 5 kilometres distant, it is decided that the furnaces shall be of 750 kilowatts under normal conditions, while during flood-time they will be put up to 850 kilowatts. With a working-tension of 5,000 volts, the power factor for these furnaces will be about 0·75.

We have had an opportunity of testing this type of furnace with as much as 1,000 kilowatts, but not yet for a sufficient length of time, as the alternator employed was too heavily laden.

The cost of these furnaces, including induction resistance, is at the present moment 18,000 kroner, or just £1,000, fully complete and capable of being immediately attached to an ordinary alternating current with a tension of

5,000 volts. The cost per kilowatt of the erection of furnaces can thus, at the present time, be put at 18 kronas, or £1, which is, of course, surprisingly low.

There is reason to believe, however, that this low cost of erection per kilowatt will at some future time be further considerably reduced. From the experience gained up to the present, it would appear that in larger works the furnaces should be made to take larger quantities of energy than 1,000 kilowatts. If, for instance, 2,000 kilowatts per furnace were absorbed, a considerable saving would be effected in the cost of erection and the working expenses.

There would also be a gain in the factor of reduction, which would probably attain to 0.8, and there is no indication—if we draw conclusions by analogy from the experiments made with from 250 to 750 kilowatts per furnace—of any loss in the output per kilowatt-year; on the contrary, a small gain might rather be expected there also.

Furnaces of 2,000 kilowatts such as these would cost, complete, between 20,000 and 22,000 kronas, or about £1,100 to £1,210, including inductive resistance; so that the cost of erection would then be from 10 to 11 kronas per kilowatt, an exceptionally low cost for the installation of electrical apparatus.

But it is now necessary to speak of the products of the process. The nitric oxide fumes which are formed in the furnaces and conducted away with the hot gases, fixate, after cooling, a further quantity of oxygen from the unconsumed part of the air, and turn into nitric peroxide; and this, when treated with water, combines to form nitric acid.

The volume of air thus treated at present in the Notodden Saltpetre Manufactory is 75,000 litres per minute; and as it contains only about 1 per cent. of nitric oxide, it will easily be understood that in discussing the question of obtaining nitric acid from the air, it has frequently been pointed out that the great rarefaction of the gases to be worked with, greatly enhances the difficulties of the problem to be solved.

The gases that come from the furnaces with a temperature of 600° to 700° C. first pass through a steam boiler, the steam of which is employed in the further manufacture of the ultimate product, calcium nitrate. In the saltpetre manufactory now in course of erection, the gases will be conducted directly through the evaporation-tank, an arrangement which implies such an important saving of heat, that the employment of coal may presumably be avoided.

After the gases are discharged from the above-mentioned steam boiler, their temperature is reduced to 200°, whereupon they are conducted through a cooling apparatus to be further cooled to about 50°. The more the gases are cooled, the more easily are they absorbed by water. The gas then enters two large oxidation-chambers with acid-proof lining. Here, as already mentioned, takes place the oxidation of the compound formed in the furnaces, nitric oxide becoming nitric peroxide, which is then conducted farther into an absorption-system, where the gas is converted into nitric acid (Fig. 8).

The absorption-system consists of two series of stone towers, whose internal dimensions are 2 × 2 × 10 metres each series containing five towers, two of granite and two of sandstone, filled with pieces of quartz, over which water, and the nitric acid formed, are made to trickle, while the fifth tower in each series is filled with ordinary bricks, over which trickles milk of lime. The milk of lime quickly absorbs the rarefied nitrous gases remaining, and is converted into a compound of calcium nitrate and calcium nitrite.

The first tower yields a 50 per cent. nitric acid, the second about 25 per cent., the third 15 per cent., and the fourth 5 per cent. The liquids from the

fourth tower are raised by compressed air to the top of the third, those from the third to the second, and those from the second to the first, thus gradually increasing in concentration up to 50 per cent., at which density the acid is conducted into a series of open granite tanks, where it is temporarily stored.

Some of this acid is employed in the decomposition of the nitrate-nitrite combination obtained by absorption by milk of lime. By the addition of nitric acid, the nitrous anhydride contained in the nitrite is driven out, and carried back to the system of towers.

The solution resulting from this, containing pure calcium nitrate, is carried, together with the rest of the stored-up acid, into another series of granite tanks, where this mixture of acid and acetous calcium nitrate lye, reacting on ordinary limestone, is converted into a solution of neutral calcium nitrate. This neutral lye is carried farther into vaporisation-chambers of iron, where it is vaporised to a boiling-point of 145°C ., answering to a concentration of from 75 to 80 per cent. of calcium nitrate, containing about 13.5 per cent. of nitrogen. This substance is then run into iron drums containing about 200 litres, where it congeals, and in that form appears on the market.

Instead of vaporising the calcium nitrate right to a boiling-point of 145° , it may be allowed to crystallise after being vaporised to a boiling-point of 120°C . The crystallised calcium nitrate is treated centrifugally, when a crystalline substance is obtained as the final product, which is mainly used commercially as a fertiliser. Its composition is $\text{Ca}(\text{NO}_3)_2 + 4\text{H}_2\text{O}$, and is a salt with hygroscopic properties. In order, therefore, to make the salt more suitable for a manure, it is converted into basic nitrate, which keeps dry, thus allowing of its being scattered with a sowing-machine. For the suggestion of basic nitrate we are indebted to Dr. Rudolph Messel, of London.

A number of manuring experiments with calcium nitrate have been made at various agricultural institutes. The results show that lime saltpetre is quite as good as the natural saltpetre, and on sandy soil even superior to it. This last fact must be ascribed to the importance of the lime contained in the saltpetre to plants in soil that is so deficient in lime.

In order to obtain a satisfactory idea of the degree of success attending the solution of the nitrogen problem, it is necessary to know approximately the cost of production of calcium nitrate produced by the process here described.

The present cost is hardly likely to be published, but there are already available various official data from which fairly definite conclusions may be drawn.

At the opening of the new Chémico-Technical Institute at the Royal Technical College in Berlin, the Director of the Institute (Professor Otto N. Witt) spoke of the utilisation of atmospheric nitrogen.* In doing so he gave a detailed description of the Birkeland-Eyde process, which he knew from personal experience, having been one of the experts who visited Notodden. With regard to the practical output, he stated that, according to his observations, the yield was between 500 and 600 kilogrammes of anhydrous nitric acid per kilowatt-year.

Now, we have observed that the output of the furnaces is considerably higher than 600 kilogrammes, if it is measured by analysing samples of gas taken out, and including in the calculation the amount of air blown through the furnaces.

* *Das neue Technisch-Chémische Institut der Kóniglichen Technischen Hochschule zu Berlin*, von Dr. Otto N. Witt. Berlin, 1906.

The measurement of large volumes of air such as those in the present case requires large, expensive, accurate gas-meters. We have used a "Duplex" from the "Cie. pour la Fabrication des Compteurs et Matériel d'usine a Gaz" of Paris, which can take a maximum of about 21,000 litres per minute. By special test-determinations, this meter, after being mounted in a separate little building, has proved to be correct to within $\frac{1}{2}$ per cent.

The reason of the considerable difference observed between the output of the furnaces and the practical output has not yet been made quite clear, and investigations into this matter are therefore still being persevered with.

In the estimate for the new factory of about 27,000 electric H.P. at Notodden by a commission of famous foreign scientists, among whom we may mention Grandeau, Schloesing, Silvanus P. Thompson,* Turrettini, and Otto N. Witt, a practical output of 500 kilogrammes of anhydrous nitric acid per kilowatt-year has been taken for granted.

In the Prospectus issued on the formation of the Company that now owns the works just named it was stated that the cost of production per ton of calcium nitrate, containing 13.2 per cent. of nitrogen, would be 72.30 kronen (£4), while the selling price per ton is put at 145.20 (£8), this having been reckoned from the present price of 1,100 kr. (about £60) per ton of combined nitrogen.

As the building of the new factory is already far advanced, there has been ample opportunity of seeing that the cost of the works has been very correctly estimated.

THEORETICAL REMARKS ON THE OXIDATION OF NITROGEN.

In 1903 Muthmann and Hofer published a treatise in which, on the principles of thermochemistry, they endeavoured to throw light upon the chemical process here treated of. They there maintained the view that the oxidation of nitrogen in electric arcs is exclusively an effect of heat, and that there appears in the arc a chemical equilibrium between oxygen, nitrogen and nitric oxide, the constants of which they tried to determine.

Most valuable investigations and attempts to come to greater clearness on the subject have since been published by Nernst,† Brode,‡ Haber||, Franz Fischer and Braehmer.§

If we adopt the views of the thermochemists, we must assume that in the electric arcs in which nitrogen is oxidised all that is wanted is the capability of greatly heating the air. It is taken for granted that the electric phenomenon itself, namely, that electric currents permeate the air, plays no part of any consequence in the nitrogen reaction. The oxidation of nitrogen is, then, no specific electric, but only a thermo-chemical action. We shall return to this point when we are discussing the degree of ionisation of the air in the electric flame.

If we take 1 kilogramme of oxygen, and mix it with 3.3 kilogrammes of nitrogen, this, according to the conceptions of modern chemistry, will no longer be just a mixture of oxygen and nitrogen. Chemical combinations of these elements form by themselves, among them nitric oxide. In this case, it is true, at an ordinary temperature, the nitric oxide formed will be an

* Professor Thompson delivered a most interesting discourse on the electric production of nitrates from the atmosphere, at the Royal Institution, Feb. 2, 1906.

† *Nachrichten d. Königl. Gesellsch. d. Wissensch.*, Göttingen, 1904.

‡ *Oxydation des Stickstoffes in der Hochspannungsflamme*, Halle, 1905.

|| *Thermodynamik technischer Gasreaktionen*, München, 1905.

§ *Berichte d. Deutschen Chem. Gesellsch.*, 1906.

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unmeasurable amount, namely, according to calculation, 10^{-20} gram, taking Guldberg-Waage's law and Van't Hoff's equation for granted.*

But when the temperature rises to $1,500^{\circ}$, $2,000^{\circ}$, and $2,500^{\circ}$, it can be proved and measured that at each temperature a certain quantity of nitric oxide is found in the gas; an equilibrium, as we say, appears, corresponding with each temperature. At $3,000^{\circ}$, for instance, an entire 5 per cent. of the composition should be nitric oxide.

One imagines that with each temperature when in equilibrium, NO is constantly being formed and constantly decomposed, so that the amount always existing in the compound is constant.

Now if our air-compound—say from $3,000^{\circ}$, and containing 5 per cent. of nitric oxide—be cooled sufficiently slowly, *e.g.*, down to 700° , the amount of nitric oxide contained will gradually diminish to a definite amount corresponding to each temperature, and it will finally sink to almost nothing, corresponding to 700° .

If, on the contrary, the cooling can take place with very great rapidity, it should be found that the 5 per cent. of nitric oxide is retained; there is no time for it to be decomposed; and when once the gas has gone down to 700° , all the changes take place with such extreme slowness that the 5 per cent. of nitric oxide is imprisoned and can be retained. It is just this instantaneous cooling of the greatly heated air that we achieve so well in our furnaces.

In all experiments in which an attempt is made to fit the theory to the experimental results obtained by the oxidation of nitrogen in the electric arc the greatest difficulty met with is in the little knowledge we possess of the temperature of the arc. In this respect we know for certain little more of the peculiar electric flames now used in technics, with thin, mobile arcs one or two yards long, than that the temperature must be extraordinarily high. Thin threads of zirconium oxide, for instance, can be melted in the high-tension electric arcs.† But the means and methods adopted in order to indicate temperatures, *e.g.*, when it is a question of the positive or negative pole of an arc between carbon-points, or of judging the temperature of the sun, will scarcely even approximately suffice for the determination of the temperature of an electric arc in atmospheric air. The basis of these methods is to measure the radiation, and examine the spectrum given by the radiating bodies, which, as such, are supposed not to be very different from a black body. But the power of the air to radiate bright rays, and even dark heat-rays, is remarkably small, even with high temperatures, a fact which may be concluded from experiments made by Hittorf, W. Siemens, and Paschen.

The arc-flame shown in Fig. 4, for instance, gives little light as compared with the large amount of energy in it. One can quite well look right into the flame, and when being photographed it was astonishingly difficult to take snapshots of it. This, of course, is also due to the rapid movements of the arcs.

I have tried to form some opinion as to the temperature conditions in the disc-flame produced, by first endeavouring to make out whether the long

* The laws of Thermochemistry probably do not hold without considerable modification for air of common temperature. Molecules of air break up and recombine under influence of many agents other than heat. All processes by which air is changed into a conductor of electricity will possibly also to a certain degree influence the chemical reactions taking place in the gas. Ozone is, for instance, produced from oxygen by rays from active radium preparations.

† Nernst, *loc. cit.* p. 1.

arcs that are always in active motion in the flame are to be considered as well-defined current-strings in the air, whose thickness, in that case, might be determined.

With this object in view, the conditions were first investigated in a small high-tension disc-flame, which was produced by spreading out the discharges from a large induction coil with mercury interrupter, into a disc in a magnetic field, just as in Du Moncel and Plücker's well-known experiment. A faintly illuminating, violet disc-flame was thus produced, more or less semi-circular, and of about 6 cm. in diameter.

The flame was very thin; with a microscope magnifying 20 times, it was judged to be about $\frac{1}{10}$ mm. It was a little thicker on the negative electrode than on the positive, which is probably accounted for by the fact that the arc-fibres of about $\frac{1}{10}$ mm. in thickness, which form the disc, cling or fix themselves more firmly with their roots to the negative electrode than to the positive. Compare the previous description on p. 103. The negative electrode also becomes warmer than the positive. In this experiment the electrodes were formed of 3 mm. thick brass wire.

In order to test the thickness of the arcs, small pieces of thin tissue paper were quickly inserted in the flame. Holes were pierced in these by the arcs, several arcs in succession often going through the same hole in the paper, which then became larger than the others. Fig. 9 shows a photograph of three such pieces of paper about five times enlarged: No. 1 taken close to the positive electrode, No. 2 in the middle, and No. 3 close to the negative electrode. The holes show diameters of from $\frac{1}{80}$ to $\frac{1}{7}$ of a millimetre.

It was proved by these experiments that the arcs, which could attain a length of about 10 cm., remained in the air everywhere in the form of very fine threads, of a thickness of about $\frac{1}{10}$ of a millimetre.

I have now made further endeavours to obtain some knowledge of the thickness of the arcs forming the flames in our furnaces, partly by measuring the size of the marks produced on the electrodes under various conditions, and partly by taking instantaneous photographs of the flames.

The marks of the arcs were taken by screwing new electrodes—immediately after the flame had begun to play upon them—as quickly as possible apart from one another, so as to extinguish the flame again. Of course, in these experiments, some rapidity is required, as the arcs record their marks 50 times per second on each side of the electrodes. In this way I have succeeded in obtaining a number of good arc-prints from various flames, from which it is easily demonstrated that even with flames of great energy the arcs *issue* from the electrodes as fine arc-threads.

Fig. 10 shows positive and negative arc-prints on electrodes for a flame of 500 kilowatts. The pieces of the electrode are photographed in their actual size. The diameter of the flame was about 140 cm., and the strength of the current employed 150 amperes.

It will be seen that the positive arc-prints are continuous bands of about 0.5 mm. in width, while the negative arc-prints consist chiefly of very close series of round spots about 0.6 mm. in diameter.

Fig. 11 is a photograph of the disc-flame of 500 kilowatts, taken in $\frac{1}{3}$ of a second parallel to the electrodes, looking in towards the centre of the furnace, and in the plane of the disc-flame.

By comparing the thickness of the arc-disc with that of the electrode, which is 15 mm., it may be concluded that the former is about 40 mm. thick.

The arcs that form the disc thus have in the air a considerable width of section as compared with the arc-prints on the electrodes.

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Probably carriers of different kinds are at work in carrying the negative electricity into the flame from the small hot spots on the negative electrodes. If we assume that near these spots positive and negative ions—travelling with velocities whose sum is V and charge e of constant number n (of either sign) per c.c.—carry the current, then :—

$$i = V n e.$$

Now i was 150 amperes through a circular spot of 0.6 mm. in diameter, thus about 1.59×10^{14} electrostatic units was passing per square centimetre. For e we take the charge carried by an ion according to the last determination of J. J. Thomson : $e = 3.4 \times 10^{-10}$ E.S. units. Now even if we put n equal to 2.8×10^{18} , approximately the number of molecules in 1 c.c. of air at standard pressure and $3,200^\circ$ C. (compare the following), we find that V must be equal to 1.7×10^5 cm./sec. The greatest value which has been observed for the negative ions at atmospheric pressure is the value obtained by H. A. Wilson in the case of flames at a temperature of about $2,000^\circ$ C., and is equal to 1,000 cm./sec. for a potential gradient of 1 volt per centimetre. It results from this that the velocity at the ions near the negative electrode must be exceedingly large, for n is certainly taken much too high in the above calculation. The great velocity of the negative ions at this high temperature points to the conclusion that the negative ions start as electrons and gradually get loaded by molecules condensing round them ; at temperatures as high as $3,200^\circ$ C. the time they exist as free electrons is an appreciable fraction of their life ; while they are free corpuscles they have an exceedingly large velocity, which they gradually lose in producing ionisation in the air by collision.*

In the long arcs in the air there is reason to believe that the current-density along the axis of the arc is greater than through the rest of the section, and that the arc's comparatively large section is a consequence of diffusion phenomena. The rate of diffusion in a radial direction reckoned transversely away from the axis of the arc must be enormous with the differences of temperature in question here.

It is certainly this diffusion of hot air out from the arc, and of cold air into it, which in the first place determines the temperature of our flame.

It is also certainly this volume of air that is thus treated directly by the arcs that takes up the greater part of the energy of the flame in the form of heat. As already mentioned, the cooled electrodes take up only about 7.5 per cent. of the energy of the flame, and the heat radiated directly from the arcs can hardly be relatively great. I have not made measurements, but I conclude this from the fact that one is able to look right into a flame of 750 kilowatts from a distance of a couple of yards, even when the eye is in the plane of the disc-flame.

For use in the following calculations I have estimated the loss by radiation in the flame approximately to equal the loss of energy in the electrodes, so as to make the total loss equal to one-sixth of the electric energy. This is, of course, a very arbitrary estimate, but it can hardly be so wrong as really to disturb the results of the calculations. It may be useful to remember in this connection that R. Helmholtz has measured the radiation from a hydrogen flame, and found it to be 3.63 per cent. of the combustion heat generated.

In order to compare the amount of nitric oxide formed per minute in our furnaces with the amount of NO that should be formed in the electric flames

* J. J. Thomson, *Conduction of Electricity through Gases*, Camb. Univ. Press, 1903, p. 204.

according to the laws of thermochemistry, it will be necessary for us to take our bearings with regard to the temperature of the flame, as this means, in a certain sense, an average temperature.

With this object in view, and as a starting-point for the following calculations, I select a series of experiments made a year ago at our trial station at Arenal with a 300-kilowatt furnace. During several days' continuous working the energy of the furnace was kept very exactly at 300 kilowatts, while 12,500 litres of air (reduced to zero temperature and standard pressure) were blown through the furnace per minute. The outflowing gases had a temperature of 700° C., and contained a volume percentage of 1.07 of NO, which answers to 179 grammes of NO per minute.

Various experiments have been made with about the same energy in the furnace, the air blown in per minute having varied from 40 litres per kilowatt to 80 litres, without making the output vary appreciably.

Experiments have also been made with various potentials from 2,500 volts up to 7,500 volts, without making any essential change in the output.

As already mentioned, the arc-disc imparts five-sixths of its energy to the gas that is treated directly. This gas therefore absorbs 60,000 gramme-calories per second.

It is assumed, moreover, that the air near the arc, which is brought into the flame by diffusion, or is treated directly by the flame, has a temperature of 700° C. immediately before it is taken up into the arc.

Further, with regard to the heat-capacity of the gases, it is assumed that the mean specific heat C_p for a mol. of permanent gases may approximately be expressed as follows :—

$$C_p = 6.8 + 0.0006.t^*$$

In order to obtain a general idea of the output of NO per minute that would be theoretically probable under these assumptions, I have calculated the output for various assumed temperatures in the flame, taking as my starting-point Nernst's equation :—

$$\log. \frac{x}{\sqrt{(79.2 - \frac{x}{2})(20.8 - \frac{x}{2})}} = \log. 0.0249 - 2.141 \frac{2200 - T}{T} \dagger$$

The result of these calculations, and a statement of the calculated volume of gas treated by the flame per second with each temperature, will be found in the following table :—

	2,500° C.	3,200°	4,200°	5,200°	6,200°	8,200°
Number of grammes of NO per minute ...	187	264	311	333	321	274
Volume percentage of NO	2.7	5.6	10	14.7	18.4	23.6
Number of litres of gas in the flame per second	880	747	634	564	516	449

* See Haber, *loc. cit.* p. 251.

† *Loc. cit.* p. 15.

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This table is calculated upon the assumption that the arc's influence upon the air has been sufficiently long to allow of the establishment of an equilibrium, and that the cooling of the gases treated has thereupon taken place so rapidly that the nitric oxide formed has not decomposed to any appreciable extent.

It will be seen from the table that the output of NO per minute with $2,500^{\circ}$ C. is 187 grammes, while the actual output from the furnace was 179 grammes. It will be seen, moreover, that the theoretical output with an inconceivably high temperature might also be of the same magnitude.

That the temperature of the flame should only be $2,500^{\circ}$ C. is a result, however, that seems to be a good deal too low; for according to Nernst, the rate of reaction at this temperature is so small that the chemical equilibrium can scarcely have appeared at all in those gases that are in the arcs themselves only for a very short space of time.

For the lengths of time within which half the possible NO concentration is formed by heating of the air, Nernst has deduced the following values:—

With $1,200^{\circ}$, very long.
 With $1,538^{\circ}$, 97 seconds.
 With $1,737^{\circ}$, 3·5 seconds.
 With $2,600^{\circ}$, 0·018 second.

The length of time for 50 per cent. of NO to appear with $2,500^{\circ}$ C. would thus be about 0·02 second. In this time, however, *a whole arc-disc is formed*, so that the air in our furnaces is not heated nearly so long in the arcs themselves.

The rates of reaction given by Nernst may possibly be too low, but it is most probable that the temperature of the arc is considerably higher than $2,500^{\circ}$.

With a temperature of $3,200^{\circ}$, 264 grammes of NO should be formed per minute, whereas in reality the furnace gives only 179 grammes. This difference, however, is not so great but that it can well be explained by the assumption that the equilibrium in the furnace is not quite established, or that the NO formed in the arcs has again been partly dissociated.*

The author assumes the average temperature in the arcs to be about $3,200^{\circ}$ C., and that the mass of the air directly treated by the arcs in this experiment was about one-fourth of that of the air blown through the furnace. The remaining three-fourths of the air is necessary for cooling that portion directly heated by the arcs in the quickest possible way down to a temperature at which the nitric oxide formed remains stable.

The maximum theoretical output coincides, as will be seen from the table, with about $5,200^{\circ}$ C.

If in practice one could choose between such high temperatures, it would be most natural to try to get up to about $4,000^{\circ}$ C., as it is probable that the radiation and other losses consequent on such enormously high temperatures would displace the maximum output, so that it would correspond with a considerably lower temperature than $5,200^{\circ}$. It seems even not unreasonable to think that when we are adjusting the magnetic force by our furnaces so as to give their highest output, we then arrive very closely at the best temperature conditions that may practically be obtained.

It may be interesting to compare the number of litres of gas that,

* In Nernst's equation it is assumed that a volume percentage of 0·99 of NO corresponds to the absolute temperature 2,200. Perhaps this temperature, corresponding to about 1 per cent. NO, is assumed a little too low.

according to the table, are treated in the flame with the previously-mentioned instantaneous photographs showing the thickness of the arc.

According to these, the disc-flame appears to be about 35 mm. thick, with an energy of 300 kilowatts. Now fifty discs are formed per second, and their diameter is about 0.9 metre. The volume of these will be 1,113 litres per second, a result which seems to accord ill with the table. It must be remembered, however, that all the gas particles in the disc-flame are not heated equally long during the movements of the arcs; they are more or less in contact with the arcs; and in the next place, the temperature of the arcs themselves is not, of course, constant all through their section. In the centre of the section the temperature is certainly very high, and diminishes towards the peripheral parts. It is possible that the photographic plate takes comparatively much of the more faintly-glowing air-envelope round the inner part of the arc, where most of the nitrogen fixation takes place.

We can here apply a thought that was evolved by Nernst*, which clearly shows the importance of a rapid cooling of the gases treated. As the temperature from the axis of an arc falls very quickly towards the peripheral parts, the partial pressure of nitric oxide answering to the central parts of the section of the arc will be considerably higher than that answering to the periphery. It follows, therefore, that a continuous and rapid diffusion of NO will take place from the central, hottest parts of the arc, out towards the colder parts.

It is assumed in the foregoing that the arcs are always moving through new volumes of air. It is probable, however, that the ions that conduct the electric current through the gas, to some extent, at any rate, follow the movements of the arcs. We may form an approximate estimate of the order of the number of the molecules in the arc that are split up into ions.

Assuming first, for the purpose of illustration, that the 90 amperes that pass through the 300-kilowatt flame are a constant "saturation current" by uniform ionisation between two parallel plates, so that the volume of air acted upon is 747 litres, corresponding to 3,200° C. in the flame (see the table).

If q be the total rate of production of ions in the gas—

$$q = \frac{I}{e}$$

I being the current and e the charge of an ion. †

In his last determination, J. J. Thomson found that—

$$e = 3.4 \times 10^{-10} \text{ electrostatic units.}$$

From this we find that—

$$q = \frac{90 \times 3 \times 10^9}{3.4 \times 10^{-10}} = 8 \times 10^{20} \text{ per second.}$$

From experimental data given by Townsend, the number of molecules present in 1 c.c. of gas at 15° C. and standard pressure is found to be—

$$N = 3.6 \times 10^{19}.$$

Now if one molecule produces two ions, and we assume that no other molecules than those that form ions are decomposed at 3,200°, the proportion of gas ionised to the whole amount of gas heated will be about 1.8×10^{-4} . This then is not more than $\frac{1}{5556}$ of the ratio between the NO formed, according to the table, and the amount of gas heated.

Now 90 amperes is certainly very far from being the "saturation current" for gases under such conditions as these, so that the number of ions in our flame will probably be very much greater than about 10^{15} , and perhaps so

* *Boltzmann-Festschrift*, Leipzig, 1904.

† See *Radio-Activity*, by E. Rutherford, Cambridge, 1905, p. 54.

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great that the concentration of monoatomic gases (N) and (O) may be comparable with the concentration of (NO). The chemical equilibrium should then be determined between the five gases (N₂, (O₂), NO), (N) and (O), and not only between the first three of them.

Let us compare the above number with the number of ions that may be produced by pure radium of an activity of one million times that of uranium. Rutherford (*loc. cit.*) deduces from an experiment that 7×10^{11} ions per second may be produced per 1 c.c. of air at standard pressure and 15° C. It would seem not impossible with pure radium to arrive at considerably higher figures, perhaps to 10^{15} per 1 c.c. per second (*loc. cit.* p. 434).

Radium rays show chemical actions of many kinds. S. and P. Curie* have shown that rays from active radium preparations change oxygen into ozone. I do not know whether traces of NO can be detected in air ionised by pure radium, in a way corresponding to the ordinary "hot-cold" treatment of air in the production of NO, but if so, it would be very interesting to find out whether the same concentration of NO is formed when the air is ionised by radium as when it is ionised to the same degree by heat.

If that is the case, the proportion of gas ionised to the whole amount of gas will be of determinative importance to the chemical equilibrium in gas compounds.