

Argon, a New Constituent of the Atmosphere

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Phil. Trans. R. Soc. Lond. A 1895 **186**, 187-241

doi: 10.1098/rsta.1895.0006

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VI. *Argon, a New Constituent of the Atmosphere.*By Lord RAYLEIGH, *Sec. R.S.*, and Professor WILLIAM RAMSAY, *F.R.S.*

Received and Read January 31, 1895.

“Modern discoveries have not been made by large collections of facts, with subsequent discussion, separation, and resulting deduction of a truth thus rendered perceptible. A few facts have suggested an *hypothesis*, which means a *supposition*, proper to explain them. The necessary results of this supposition are worked out, and then, and not till then, other facts are examined to see if their ulterior results are found in Nature.”—DE MORGAN, “A Budget of Paradoxes,” ed. 1872, p. 55.

1. *Density of Nitrogen from Various Sources.*

IN a former paper* it has been shown that nitrogen extracted from chemical compounds is about one-half per cent. lighter than “atmospheric nitrogen.”

The mean numbers for the weights of gas contained in the globe used were as follows:—

	grams.
From nitric oxide	2·3001
From nitrous oxide	2·2990
From ammonium nitrite	2·2987

while for “atmospheric” nitrogen there was found—

By hot copper, 1892	2·3103
By hot iron, 1893	2·3100
By ferrous hydrate, 1894	2·3102

At the suggestion of Professor THORPE, experiments were subsequently tried with nitrogen liberated from *urea* by the action of sodium hypobromite. The carbon and hydrogen of the urea are supposed to be oxidized by the reaction to CO₂ and H₂O, the former of which would be retained by the large excess of alkali employed. It was accordingly hoped that the gas would require no further purification than drying. If it proved to be light, it would at any rate be free from the suspicion of containing hydrogen.

* RAYLEIGH, “On an Anomaly encountered in Determinations of the Density of Nitrogen Gas,” ‘Proc. Roy. Soc.’ vol. 55, p. 340, 1894.

The hypobromite was prepared from commercial materials in the proportions recommended for the analysis of urea—100 grams. caustic soda, 250 cub. centims. water, and 25 cub. centims. of bromine. For our purpose about one and a half times the above quantities were required. The gas was liberated in a bottle of about 900 cub. centims. capacity, in which a vacuum was first established. The full quantity of hypobromite solution was allowed to run in slowly, so that any dissolved gas might be at once disengaged. The urea was then fed in, at first in a dilute condition, but, as the pressure rose, in a 10 per cent. solution. The washing out of the apparatus, being effected with gas in a highly rarefied state, made but a slight demand upon the materials. The reaction was well under control, and the gas could be liberated as slowly as desired.

In the first experiment, the gas was submitted to no other treatment than slow passage through potash and phosphoric anhydride, but it soon became apparent that the nitrogen was contaminated. The "inert and inodorous" gas attacked vigorously the mercury of the Töpler pump, and was described as smelling like a dead rat. As to the weight, it proved to be in excess even of the weight of atmospheric nitrogen.

The corrosion of the mercury and the evil smell were in great degree obviated by passing the gas over hot metals. For the fillings of June 6, 9, 13, the gas passed through a short length of tube containing copper in the form of fine wire, heated by a flat Bunsen burner, then through the furnace over red-hot iron, and back over copper oxide. On June 19 the furnace tubes were omitted, the gas being treated with the red-hot copper only. The results, reduced so as to correspond with those above quoted, were—

June 6	2·2978
„ 9	2·2987
„ 13	2·2982
„ 19	2·2994
Mean	2·2985

Without using heat it has not been found possible to prevent the corrosion of the mercury. Even when no urea is employed, and air simply bubbled through the hypobromite solution is allowed to pass with constant shaking over mercury contained in a U tube, the surface of the metal was soon fouled. When *hypochlorite* was substituted for *hypobromite* in the last experiment there was a decided improvement, and it was thought desirable to try whether the gas prepared from hypochlorite and urea would be pure on simple desiccation. A filling on June 25 gave as the weight 2·3343, showing an excess of 36 mgs., as compared with other chemical nitrogen, and of about 25 mgs. as compared with atmospheric nitrogen. A test with alkaline pyrogallate appeared to prove the absence from this gas of free oxygen, and only a trace of carbon could be detected when a considerable quantity of the gas was passed over red-hot cupric oxide into solution of baryta.

Although the results relating to urea nitrogen are interesting for comparison with that obtained from other nitrogen compounds, the original object was not attained on account of the necessity of retaining the treatment with hot metals. We have found, however, that nitrogen from ammonium nitrite may be prepared without the employment of hot tubes, whose weight agrees with that above quoted. It is true that the gas smells slightly of ammonia, easily removable by sulphuric acid, and apparently also of oxides of nitrogen. The solution of potassium nitrite and ammonium chloride was heated in a water-bath, of which the temperature rose to the boiling-point only towards the close of operations. In the earlier stages the temperature required careful watching in order to prevent the decomposition taking place too rapidly. The gas was washed with sulphuric acid, and after passing a Nessler test, was finally treated with potash and phosphoric anhydride in the usual way. The following results have been obtained:—

July 4	2·2983
„ 9	2·2989
„ 13	2·2990
	Mean
	2·2987

It will be seen that in spite of the slight nitrous smell there is no appreciable difference in the densities of gas prepared from ammonium nitrite with and without the treatment by hot metals. The result is interesting, as showing that the agreement of numbers obtained for chemical nitrogen does not depend upon the use of a red heat in the process of purification.

The five results obtained in more or less distinct ways for chemical nitrogen stand thus:—

From nitric oxide	2·3001
From nitrous oxide	2·2990
From ammonium nitrite purified at a red heat	2·2987
From urea	2·2985
From ammonium nitrite purified in the cold	2·2987
	Mean
	2·2990

These numbers, as well as those above quoted for “atmospheric nitrogen,” are subject to a correction (additive)* of ·0006 for the shrinkage of the globe when exhausted.† If they are then multiplied in the ratio of 2·3108 : 1·2572, they will express the weights of the gas in grams. per litre. Thus, as regards the mean numbers, we find as the weight per litre under standard conditions of chemical nitrogen 1·2511, that of atmospheric nitrogen being 1·2572.

[* In the Abstract of this paper (‘Proc. Roy. Soc.’ vol. 57, p. 265) the correction of ·0006 was erroneously treated as a deduction.—April, 1895.]

† RAYLEIGH, “On the Densities of the Principal Gases,” ‘Proc. Roy. Soc.’ vol. 53, p. 134, 1893.

It is of interest to compare the density of nitrogen obtained from chemical compounds with that of oxygen. We have $N_2 : O_2 = 2.2996 : 2.6276 = 0.87517$; so that if $O_2 = 16$, $N_2 = 14.003$. Thus, when the comparison is with chemical nitrogen, the ratio is very nearly that of 16 : 14. But if "atmospheric nitrogen" be substituted, the ratio of small integers is widely departed from.

The determination by STAS of the atomic weight of nitrogen from synthesis of silver nitrate is probably the most trustworthy, inasmuch as the atomic weight of silver was determined with reference to oxygen with the greatest care, and oxygen is assumed to have the atomic weight 16. If, as found by STAS, $Ag NO_3 : Ag = 1.57490 : 1$, and $Ag : O = 107.930 : 16$, then $N : O = 14.049 : 16$.

To the above list may be added nitrogen, prepared in yet another manner, whose weight has been determined subsequently to the isolation of the new dense constituent of the atmosphere. In this case nitrogen was actually extracted from air by means of magnesium. The nitrogen thus separated was then converted into ammonia by action of water upon the magnesium nitride, and afterwards liberated in the free state by means of calcium hypochlorite. The purification was conducted in the usual way, and included passage over red-hot copper and copper oxide. The following was the result:—

Globe empty, October 30, November 5	2.82313
Globe full, October 3152395
	2.29918
Weight of gas	2.29918

It differs inappreciably from the mean of other results, viz., 2.2990, and is of special interest as relating to gas which, at one stage of its history, formed part of the atmosphere.

Another determination with a different apparatus of the density of "chemical" nitrogen from the same source, magnesium nitride, which had been prepared by passing "atmospheric" nitrogen over ignited magnesium, may here be recorded. The sample differed from that previously mentioned, inasmuch as it had not been subjected to treatment with red-hot copper. After treating the nitride with water, the resulting ammonia was distilled off, and collected in hydrochloric acid; the solution was evaporated to dryness; the dry ammonium chloride was dissolved in water, and its concentrated solution added to a freshly prepared solution of sodium hypobromite. The nitrogen was collected in a gas-holder over water which had previously been boiled, so as at all events partially to expel air. The nitrogen passed into the vacuous globe through a solution of potassium hydroxide, and through two drying-tubes, one containing soda-lime, and the other phosphoric anhydride.

At 18.38° C. and 754.4 mgs. pressure, 162.843 cub. centims. of this nitrogen weighed 0.18963 gram. Hence:—

Weight of 1 litre at 0° C. and 760 millims. pressure . . . 1.2521 gram.

The mean result of the weight of 1 litre of "chemical" nitrogen has been found to equal 1.2511. It is therefore seen that "chemical" nitrogen, derived from "atmospheric" nitrogen, without any exposure to red-hot copper, possesses the usual density.

Experiments were also made, which had for their object to prove that the ammonia, produced from the magnesium nitride, is identical with ordinary ammonia, and contains no other compound of a basic character. For this purpose, the ammonia was converted into ammonium chloride, and the percentage of chlorine determined by titration with a solution of silver nitrate which had been standardized by titrating a specimen of pure sublimed ammonium chloride. The silver solution was of such a strength that 1 cubic centim. precipitated the chlorine from 0.001701 gram. of ammonium chloride.

1. Ammonium chloride from orange-coloured sample of magnesium nitride.

0.1106 gram. required 43.10 cub. centims. of silver nitrate = 66.35 per cent. of chlorine.

2. Ammonium chloride from blackish magnesium nitride.

0.1118 gram. required 43.6 cub. centims. of silver nitrate = 66.35 per cent. of chlorine.

3. Ammonium chloride from nitride containing a large amount of unattacked magnesium.

0.0630 gram. required 24.55 cub. centims. of silver nitrate = 66.30 per cent. of chlorine.

Taking for the atomic weights of hydrogen, $H = 1.0032$, of nitrogen, $N = 14.04$, and of chlorine, $Cl = 35.46$, the theoretical amount of chlorine in ammonium chloride is 66.27 per cent.

From these results—that nitrogen prepared from magnesium nitride obtained by passing "atmospheric" nitrogen over red-hot magnesium has the density of "chemical" nitrogen, and that ammonium chloride prepared from magnesium nitride contains practically the same percentage of chlorine as pure ammonium chloride—it may be concluded that red-hot magnesium withdraws from "atmospheric" nitrogen no substance other than nitrogen capable of forming a basic compound with hydrogen.

In a subsequent part of this paper, attention will again be called to this statement. (See addendum p. 240.)

2. *Reasons for Suspecting a hitherto Undiscovered Constituent in Air.*

When the discrepancy of weights was first encountered, attempts were naturally made to explain it by contamination with known impurities. Of these the most likely appeared to be hydrogen, present in the lighter gas, in spite of the passage over red-hot cupric oxide. But, inasmuch as the intentional introduction of hydrogen into the heavier gas, afterwards treated in the same way with cupric oxide, had no effect upon its weight, this explanation had to be abandoned; and, finally, it became

clear that the difference could not be accounted for by the presence of any known impurity. At this stage it seemed not improbable that the lightness of the gas extracted from chemical compounds was to be explained by partial dissociation of nitrogen molecules N_2 into detached atoms. In order to test this suggestion, both kinds of gas were submitted to the action of the silent electric discharge, with the result that both retained their weights unaltered. This was discouraging, and a further experiment pointed still more markedly in the negative direction. The chemical behaviour of nitrogen is such as to suggest that dissociated atoms would possess a higher degree of activity, and that, even though they might be formed in the first instance, their life would probably be short. On standing, they might be expected to disappear, in partial analogy with the known behaviour of ozone. With this idea in view, a sample of chemically-prepared nitrogen was stored for eight months. But, at the end of this time, the density showed no sign of increase, remaining exactly as at first.*

Regarding it as established that one or other of the gases must be a mixture, containing, as the case might be, an ingredient much heavier or much lighter than ordinary nitrogen, we had to consider the relative probabilities of the various possible interpretations. Except upon the already discredited hypothesis of dissociation, it was difficult to see how the gas of chemical origin could be a mixture. To suppose this would be to admit two kinds of nitric acid, hardly reconcilable with the work of STAS and others upon the atomic weight of that substance. The simplest explanation in many respects was to admit the existence of a second ingredient in air from which oxygen, moisture, and carbonic anhydride had already been removed. The proportional amount required was not great. If the density of the supposed gas were double that of nitrogen, one-half per cent. only by volume would be needed; or, if the density were but half as much again as that of nitrogen, then one per cent. would still suffice. But in accepting this explanation, even provisionally, we had to face the improbability that a gas surrounding us on all sides, and present in enormous quantities, could have remained so long unsuspected.

The method of most universal application by which to test whether a gas is pure or a mixture of components of different densities is that of diffusion. By this means GRAHAM succeeded in effecting a partial separation of the nitrogen and oxygen of the air, in spite of the comparatively small difference of densities. If the atmosphere contain an unknown gas of anything like the density supposed, it should be possible to prove the fact by operations conducted upon air which had undergone atmolysis. If, for example, the parts least disposed to penetrate porous walls were retained, the "nitrogen" derived from it by the usual processes should be heavier than that derived in like manner from unprepared air. This experiment, although in view from the first, was not executed until a later stage of the inquiry (§ 6), when results were

* RAYLEIGH, 'Proc. Roy. Soc.,' vol. 55, p. 344, 1894.

obtained sufficient of themselves to prove that the atmosphere contains a previously unknown gas.

But although the method of diffusion was capable of deciding the main, or at any rate the first question, it held out no prospect of isolating the new constituent of the atmosphere, and we therefore turned our attention in the first instance to the consideration of methods more strictly chemical. And here the question forced itself upon us as to what really was the evidence in favour of the prevalent doctrine that the inert residue from air after withdrawal of oxygen, water, and carbonic anhydride, is all of one kind.

The identification of "phlogisticated air" with the constituent of nitric acid is due to CAVENDISH, whose method consisted in operating with electric sparks upon a short column of gas confined with potash over mercury at the upper end of an inverted U-tube.* This tube (M) was only about $\frac{1}{10}$ inch in diameter, and the column of gas was usually about 1 inch in length. After describing some preliminary trials, CAVENDISH proceeds:—"I introduced into the tube a little soap-lees (potash), and then let up some dephlogisticated† and common air, mixed in the above mentioned proportions which rising to the top of the tube M, divided the soap-lees into its two legs. As fast as the air was diminished by the electric spark, I continued adding more of the same kind, till no further diminution took place: after which a little pure dephlogisticated air, and after that a little common air, were added, in order to see whether the cessation of diminution was not owing to some imperfection in the proportion of the two kinds of air to each other; but without effect. The soap-lees being then poured out of the tube, and separated from the quicksilver, seemed to be perfectly neutralised, and they did not at all discolour paper tinged with the juice of blue flowers. Being evaporated to dryness, they left a small quantity of salt, which was evidently nitre, as appeared by the manner in which paper, impregnated with a solution of it, burned."

Attempts to repeat CAVENDISH'S experiment in CAVENDISH'S manner have only increased the admiration with which we regard this wonderful investigation. Working on almost microscopical quantities of material, and by operations extending over days and weeks, he thus established one of the most important facts in chemistry. And what is still more to the purpose, he raises as distinctly as we

* "Experiments on Air," 'Phil. Trans.,' vol. 75, p. 372, 1785.

[† The explanation of combustion in CAVENDISH'S day was still vague. It was generally imagined that substances capable of burning contained an unknown principle, to which the name 'phlogiston' was applied, and which escaped during combustion. Thus, metals and hydrogen and other gases were said to be 'phlogisticated' if they were capable of burning in air. Oxygen being non-inflammable was named 'dephlogisticated air,' and nitrogen, because it was incapable of supporting combustion or life was named by PRIESTLEY 'phlogisticated air,' although up till CAVENDISH'S time it had not been made to unite with oxygen.

The term used for oxygen by CAVENDISH is 'dephlogisticated air,' and for nitrogen, 'phlogisticated air.'—April, 1895.]

could do, and to a certain extent resolves, the question above suggested. The passage is so important that it will be desirable to quote it at full length.

“As far as the experiments hitherto published extend, we scarcely know more of the phlogisticated part of our atmosphere than that it is not diminished by lime-water, caustic alkalis, or nitrous air; that it is unfit to support fire or maintain life in animals; and that its specific gravity is not much less than that of common air; so that, though the nitrous acid, by being united to phlogiston, is converted into air possessed of these properties, and consequently, though it was reasonable to suppose, that part at least of the phlogisticated air of the atmosphere consists of this acid united to phlogiston, yet it was fairly to be doubted whether the whole is of this kind, or whether there are not in reality many different substances confounded together by us under the name of phlogisticated air. I therefore made an experiment to determine whether the whole of a given portion of the phlogisticated air of the atmosphere could be reduced to nitrous acid, or whether there was not a part of a different nature to the rest which would refuse to undergo that change. The foregoing experiments indeed in some measure decided this point, as much the greatest part of the air let up into the tube lost its elasticity; yet as some remained unabsorbed it did not appear for certain whether that was of the same nature as the rest or not. For this purpose I diminished a similar mixture of dephlogisticated and common air, in the same manner as before, till it was reduced to a small part of its original bulk. I then, in order to decompose as much as I could of the phlogisticated air which remained in the tube, added some dephlogisticated air to it and continued the spark until no further diminution took place. Having by these means condensed as much as I could of the phlogisticated air, I let up some solution of liver of sulphur to absorb the dephlogisticated air; after which only a small bubble of air remained unabsorbed, which certainly was not more than $\frac{1}{120}$ of the bulk of the phlogisticated air let up into the tube; so that, if there is any part of the phlogisticated air of our atmosphere which differs from the rest, and cannot be reduced to nitrous acid, we may safely conclude that it is not more than $\frac{1}{120}$ part of the whole.”

Although CAVENDISH was satisfied with his result, and does not decide whether the small residue was genuine, our experiments about to be related render it not improbable that his residue was really of a different kind from the main bulk of the “phlogisticated air,” and contained the gas now called argon.

CAVENDISH gives data* from which it is possible to determine the rate of absorption of the mixed gases in his experiment. The electrical machine used “was one of Mr. NAIRNE’S patent machines, the cylinder of which is $12\frac{1}{2}$ inches long and 7 in diameter. A conductor, 5 feet long and 6 inches in diameter, was adapted to it, and the ball which received the spark was placed two or three inches from another ball, fixed to the end of the conductor. Now, when the machine worked well, Mr. GILPIN supposes he got about two or three hundred sparks a minute, and the diminution of

* ‘Phil. Trans.,’ vol. 78, p. 271, 1788.

the air during the half hour which he continued working at a time varied in general from 40 to 120 measures, but was usually greatest when there was most air in the tube, provided the quantity was not so great as to prevent the spark from passing readily." The "measure" spoken of represents the volume of one grain of quicksilver, or .0048 cub. centim., so that an absorption of one cub. centim. of mixed gas per hour was about the most favourable rate. Of the mixed gas about two-fifths would be nitrogen.

3. *Methods of Causing Free Nitrogen to Combine.*

The concord between the determinations of density of nitrogen obtained from sources other than the atmosphere, having made it at least probable that some heavier gas exists in the atmosphere, hitherto undetected, it became necessary to submit atmospheric nitrogen to examination, with a view of isolating, if possible, the unknown and overlooked constituent, or it might be constituents.

Nitrogen, however, is an element which does not easily enter into direct combination with other elements; but with certain elements, and under certain conditions, combination may be induced. The elements which have been directly united to nitrogen are (*a*) boron, (*b*) silicon, (*c*) titanium, (*d*) lithium, (*e*) strontium and barium, (*f*) magnesium, (*g*) aluminium, (*h*) mercury, (*i*) manganese, (*j*) hydrogen, and (*k*) oxygen, the last two by help of an electrical discharge.

(*a.*) *Nitride of boron* was prepared by WÖHLER and DEVILLE* by heating amorphous boron to a white heat in a current of nitrogen. Experiments were made to test whether the reaction would take place in a tube of difficultly fusible glass; but it was found that the combination took place at a bright red heat to only a small extent, and that the boron, which had been prepared by heating powdered boron oxide with magnesium dust, was only superficially attacked. Boron is, therefore, not a convenient absorbent for nitrogen. [M. MOISSAN informs us that the reputation it possesses is due to the fact that early experiments were made with boron which had been obtained by means of sodium, and which probably contained a boride of that metal. —April, 1895.]

(*b.*) *Nitride of silicon*† also requires for its formation a white heat, and complete union is difficult to bring about. Moreover, it is not easy to obtain large quantities of silicon. This method was therefore not attempted.

(*c.*) *Nitride of titanium* is said to have been formed by DEVILLE and CARON,‡ by heating titanium to whiteness in a current of nitrogen. This process was not tried by us. As titanium has an unusual tendency to unite with nitrogen, it might, perhaps, be worth while to set the element free in presence of atmospheric nitrogen, with a view to the absorption of the nitrogen. This has, in effect, been already done

* 'Annales de Chimie,' (3), 52, p. 82.

† SCHUTZENBERGER, 'Comptes Rendus,' 89, 644.

‡ 'Annalen der Chemie u. Pharmacie,' 101, 360.

by WÖHLER and DEVILLE;* they passed a mixture of the vapour of titanium chloride and nitrogen over red-hot aluminium, and obtained a large yield of nitride. It is possible that a mixture of the precipitated oxide of titanium with magnesium dust might be an effective absorbing agent at a comparatively low temperature. [Since writing the above we have been informed by M. MOISSAN that titanium, heated to 800°, burns brilliantly in a current of nitrogen. It might therefore be used with advantage to remove nitrogen from air, inasmuch as we have found that it does not combine with argon.—April, 1895.]

(*d.*), (*e.*) Lithium at a dull red heat absorbs nitrogen,† but the difficulty of obtaining the metal in quantity precludes its application. On the other hand, strontium and barium, prepared by electrolysing solutions of their chlorides in contact with mercury, and subsequently removing the mercury by distillation, are said by MAQUENNE‡ to absorb nitrogen with readiness. Although we have not tried these metals for removing nitrogen, still our experience with their amalgams has led us to doubt their efficacy, for it is extremely difficult to free them from mercury by distillation, and the product is a fused ingot, exposing very little surface to the action of the gas. The process might, however, be worth a trial.

Barium is the efficient absorbent for nitrogen when a mixture of barium carbonate and carbon is ignited in a current of nitrogen, yielding cyanide. Experiments have shown, however, that the formation of cyanides takes place much more readily and abundantly at a high temperature, a temperature not easily reached with laboratory appliances. Should the process ever come to be worked on a large scale, the gas rejected by the barium will undoubtedly prove a most convenient source of argon.

(*f.*) *Nitride of magnesium* was prepared by DEVILLE and CARON (*loc. cit.*) during the distillation of impure magnesium. It has been more carefully investigated by BRIEGLEB and GEUTHER,§ who obtained it by igniting metallic magnesium in a current of nitrogen. It forms an orange-brown, friable substance, very porous, and it is easily produced at a bright red heat. When magnesium, preferably in the form of thin turnings, is heated in a combustion tube in a current of nitrogen, the tube is attacked superficially, a coating of magnesium silicide being formed. As the temperature rises to bright redness, the magnesium begins to glow brightly, and combustion takes place, beginning at that end of the tube through which the gas is introduced. The combustion proceeds regularly, the glow extending down the tube, until all the metal has united with nitrogen. The heat developed by the combination is considerable, and the glass softens; but by careful attention and regulation of the rate of the current, the tube lasts out an operation. A piece of combustion tubing of the usual length for organic analysis packed tightly with magnesium turnings, and containing

* 'Annalen der Chemie u. Pharmacie,' 73, 34.

† OUVREARD, 'Comptes Rendus,' 114, 120.

‡ OUVREARD, 'Comptes Rendus,' 114, 25, and 220.

§ 'Annalen der Chemie u. Pharmacie,' 123, 228.

about 30 grams, absorbs between seven and eight litres of nitrogen. It is essential that oxygen be excluded from the tube, otherwise a fusible substance is produced, possibly nitrate, which blocks the tube. With the precaution of excluding oxygen, the nitride is loose and porous, and can easily be removed from the tube with a rod; but it is not possible to use a tube twice, for the glass is generally softened and deformed.

(g.) *Nitride of aluminium* has been investigated by MALLETT.* He obtained it in crystals by heating the metal to whiteness in a carbon crucible. But aluminium shows no tendency to unite with nitrogen at a red heat, and cannot be used as an absorbent for the gas.

(h.) GERRESHEIM† states that he has induced combination between nitrogen and mercury; but the affinity between these elements is of the slightest, for the compound is explosive.

(i.) In addition to these, metallic manganese in a finely divided state has been shown to absorb nitrogen at a not very elevated temperature, forming a nitride of the formula Mn_5N_2 .‡

(j.) [A mixture of nitrogen with hydrogen, standing over acid, is absorbed at a fair rate under the influence of electric sparks. But with an apparatus such as that shown in fig. 1, the efficiency is but a fraction (perhaps $\frac{1}{3}$) of that obtainable when oxygen is substituted for hydrogen and alkali for acid.—April, 1895.]

4. *Early Experiments on sparking Nitrogen with Oxygen in presence of Alkali.*

In our earliest attempts to isolate the suspected gas by the method of CAVENDISH, we used a RUHMKORFF coil of medium size actuated by a battery of five Grove cells. The gases were contained in a test-tube A, fig. 1, standing over a large quantity of weak alkali B, and the current was conveyed in wires insulated by U-shaped glass tubes CC passing through the liquid round the mouth of the test tube. The inner platinum ends DD of the wires were sealed into the glass insulating tubes, but reliance was not placed upon these sealings. In order to secure tightness in spite of cracks, mercury was placed in the bends. This disposition of the electrodes complicates the apparatus somewhat and entails the use of a large depth of liquid in order to render possible the withdrawal of the tubes, but it has the great advantage of dispensing with sealing electrodes of platinum into the principal vessel, which might give way and cause the loss of the experiment at the most inconvenient moment. With the given battery and coil a somewhat short spark, or arc, of about 5 millims. was found to be more favourable than a longer one. When the mixed gases were in the right proportion, the rate of absorption was about 30 cub. centims.

* 'Journ. Chem. Soc.,' 1876, vol. 2, p. 349.

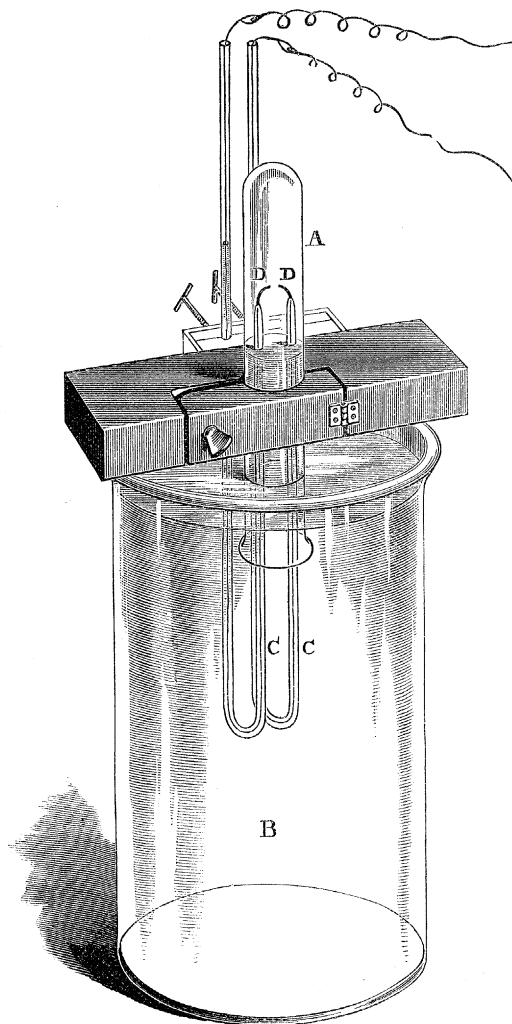
† 'Annalen der Chemie u. Pharmacie,' 195, 373.

‡ O. PREHLINGER, 'Monatsh. f. Chemie,' 15, 391.

per hour, or 30 times as fast as CAVENDISH could work with the electrical machine of his day.

To take an example, one experiment of this kind started with 50 cub. centims. of air. To this, oxygen was gradually added until, oxygen being in excess, there was no perceptible contraction during an hour's sparking. The remaining gas was then transferred at the pneumatic trough to a small measuring vessel, sealed by mercury,

Fig. 1.



in which the volume was found to be 1.0 cub. centim. On treatment with alkaline pyrogallate, the gas shrank to .32 cub. centim. That this small residue could not be nitrogen was argued from the fact that it had withstood the prolonged action of the spark, although mixed with oxygen in nearly the most favourable proportion.

The residue was then transferred to the test-tube with an addition of another 50 cub. centims. of air, and the whole worked up with oxygen as before. The residue was now 2.2 cub. centims., and, after removal of oxygen, .76 cub. centim.

Although it seemed almost impossible that these residues could be either nitrogen or hydrogen, some anxiety was not unnatural, seeing that the final sparking took place under somewhat abnormal conditions. The space was very restricted, and the temperature (and with it the proportion of aqueous vapour) was unduly high. But any doubts that were felt upon this score were removed by comparison experiments in which the whole quantity of air operated on was very small. Thus, when a mixture of 5 cub. centims. of air with 7 cub. centims. of oxygen was sparked for one hour and a quarter, the residue was .47 cub. centim., and, after removal of oxygen, .06 cub. centim. Several repetitions having given similar results, it became clear that the final residue did not depend upon anything that might happen when sparks passed through a greatly reduced volume, *but was in proportion to the amount of air operated upon.*

No satisfactory examination of the residue which refused to be oxidised could be made without the accumulation of a larger quantity. This, however, was difficult of attainment at the time in question. The gas seemed to rebel against the law of addition. It was thought that the cause probably lay in the solubility of the gas in water, a suspicion since confirmed. At length, however, a sufficiency was collected to allow of sparking in a specially constructed tube, when a comparison with the air spectrum taken under similar conditions proved that, at any rate, the gas was not nitrogen. At first scarcely a trace of the principal nitrogen lines could be seen, but after standing over water for an hour or two these lines became apparent.

[The apparatus shown in fig. 1 has proved to be convenient for the purification of small quantities of argon, and for determinations of the amount of argon present in various samples of gas, *e.g.*, in the gases expelled from solution in water. To set it in action an alternating current is much to be preferred to a battery and break. At the Royal Institution the primary of a small RUHMKORFF was fed from the 100-volt alternating current supply, controlled by two large incandescent lamps in series with the coil. With this arrangement the voltage at the terminals of the secondary, available for starting the sparks, was about 2000, and could be raised to 4000 by plugging out one of the lamps. With both lamps in use the rate of absorption of mixed gases was 80 cub. centims. per hour, and this was about as much as could well be carried out in a test-tube. Even with this amount of power it was found better to abandon the sealings at D. No inconvenience arises from the open ends, if the tubes are wide enough to ensure the liberation of any gas included over the mercury when they are sunk below the liquid.

The power actually expended upon the coil is very small. When the apparatus is at work the current taken is only 2.4 amperes. As regards the voltage, by far the greater part is consumed in the lamps. The efficient voltage at the terminals of the primary coil is best found indirectly. Thus, if A be the current in amperes, V the total voltage, V_1 the voltage at the terminals of the coil, V_2 that at the terminals of the lamps, the watts used are*

* AYRTON and SUMPNER, 'Proc. Roy. Soc.,' vol. 49, p. 427, 1891.

$$W = \frac{A}{2V_2} (V^2 - V_2^2 - V_1^2).$$

In the present case a CARDEW voltmeter gave $V = 90\frac{1}{2}$, $V_2 = 88$; and V_1^2 in the formula may be neglected. Thus,

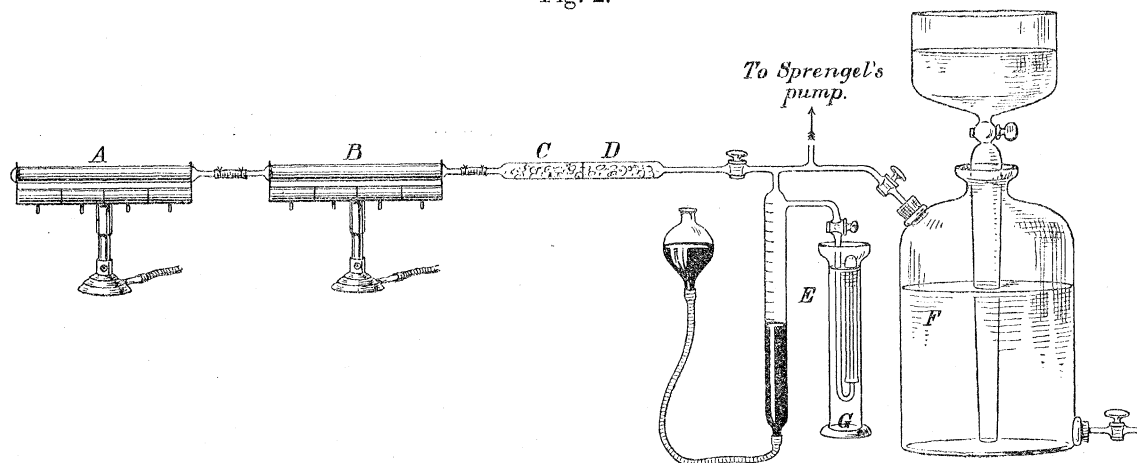
$$\begin{aligned} W &= \frac{A}{2V_2} (V + V_2)(V - V_2) = A(V - V_2) \\ &= 2.4 \times 2.5 = 6.0 \text{ approximately.} \end{aligned}$$

The work consumed by the coil when the sparks are passing is, thus, less than $\frac{1}{100}$ of a horse-power; but, in designing an apparatus, it must further be remembered that in order to maintain the arc, a pretty high voltage is required at the terminals of the secondary when no current is passing in it.—April, 1895.]

5. *Early Experiments on Withdrawal of Nitrogen from Air by means of Red-hot Magnesium.*

It having been proved that nitrogen, at a bright red heat, was easily absorbed by magnesium, best in the form of turnings, an attempt was successfully made to remove that gas from the residue left after eliminating oxygen from air by means of red-hot copper.

Fig. 2.



The preliminary experiment was made in the following manner:—A combustion tube, A, was filled with magnesium turnings, packed tightly by pushing them in with a rod. This tube was connected with a second piece of combustion tubing, B, by means of thick-walled india-rubber tubing, carefully wired; B contained copper oxide, and, in its turn, was connected with the tube CD, one-half of which contained soda-lime, previously ignited to expel moisture, while the other half was filled with phosphoric anhydride. E is a measuring vessel, and F is a gas-holder containing “atmospheric nitrogen.”

In beginning an experiment, the tubes were heated with long-flame burners, and pumped empty; a little hydrogen was formed by the action of the moisture on the metallic magnesium; it was oxidised by the copper oxide and absorbed by the phosphoric pentoxide. A gauge attached to the SPRENGEL'S pump, connected with the apparatus, showed when a vacuum had been reached. A quantity of nitrogen was then measured in E, and admitted into contact with the red-hot magnesium. Absorption took place, rapidly at first and then slowly, as shown by the gauge on the SPRENGEL'S pump. A fresh quantity was then measured and admitted, and these operations were repeated until no more could be absorbed. The system of tubes was then pumped empty by means of the SPRENGEL'S pump, and the gas was collected. The magnesium tube was then detached and replaced by another. The unabsorbed gas was returned to the measuring-tube by a device shown in the figure (G) and the absorption recommenced. After 1094 cub. centims. of gas had been thus treated, there was left about 50 cub. centims. of gas, which resisted rapid absorption. It still contained nitrogen, however, judging by the diminution of volume which it experienced when allowed to stand in contact with red-hot magnesium. Its density was, nevertheless, determined by weighing a small bulb of about 40 cub. centims. capacity, first with air, and afterwards with the gas. The data are these:—

	gram.
(a.) Weight of bulb and air — that of glass counterpoise . . .	0·8094
,, ,, alone — that of glass counterpoise . . .	0·7588
,, air	0·0506
(b.) Weight of bulb and gas — that of glass counterpoise . . .	0·8108
,, ,, alone — that of glass counterpoise . . .	0·7588
,, gas	0·0520

Taking as the weight of a litre of air, 1·29347 grms., the mean of the latest results, and of oxygen (= 16) 1·42961 grms.,* the density of the residual gas is 14·88.

* The results on which this and the subsequent calculations are based are as follows (the weights are those of 1 litre):—

	Air.	Oxygen.	Nitrogen.	Hydrogen.
REGNAULT	1·29349	1·43011	1·25647	0·08988
VON JOLLY	1·29383	1·42971	1·25819	
LEDUC	1·29330	1·42910	1·25709	0·08985
RAYLEIGH	1·29327	1·42952	1·25718	0·09001

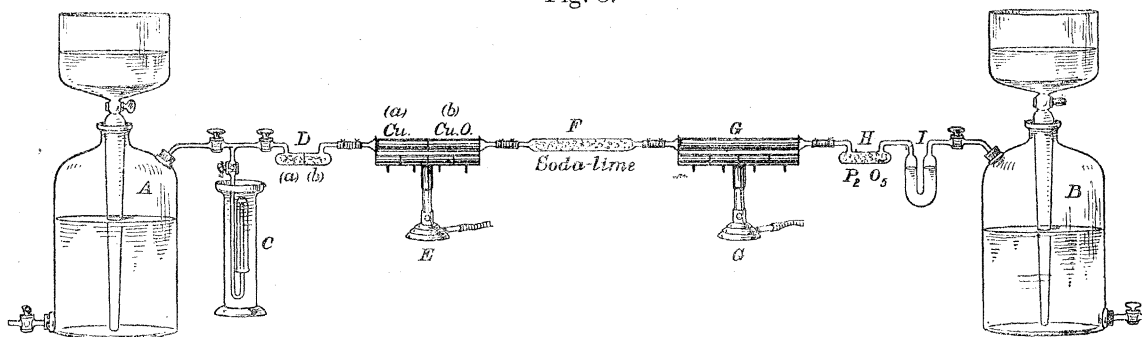
REGNAULT'S numbers have an approximate correction applied to them by CRAFTS. The mean of these
M DCCCXCV.—A.

This result was encouraging, although weighted with the unavoidable error attaching to the weighing of a very small amount. Still the fact remains that the supposed nitrogen was heavier than air. It would hardly have been possible to make a mistake of 2·7 milligrams.

It is right here to place on record the fact that this first experiment was to a great extent carried out by Mr. PERCY WILLIAMS, to whose skill in manipulation and great care its success is due, and to whom we desire here to express our thanks.

Experiments were now begun on a larger scale, the apparatus employed being shown in figs. 3 and 4.

Fig. 3.



A and B are large glass gas-holders of about 10 litres capacity. C is an arrangement by which gas could be introduced at will into the gas-holder A, either by means of an india-rubber tube slipped over the open end of the U-tube, or, as shown in the figure, from a test-tube. The tube D was half filled with soda-lime (a), half with phosphoric anhydride (b). Similarly, the tube E, which was kept at a red heat by means of the long-flame burner, was filled half with very porous copper (a), reduced from dusty oxide by heating in hydrogen, half with copper oxide in a granular form (b). The next tube, F, contained granular soda-lime, while G contained magnesium turn-

numbers is taken, that of REGNAULT for nitrogen being omitted, as there is reason to believe that his specimen was contaminated with hydrogen.

Air.	Oxygen.	Nitrogen.	Hydrogen.
1·29347	1·42961	1·25749	0·08991

This ratio gives for air the composition by volume—

Oxygen 20·91 per cent.
Nitrogen 79·09 „

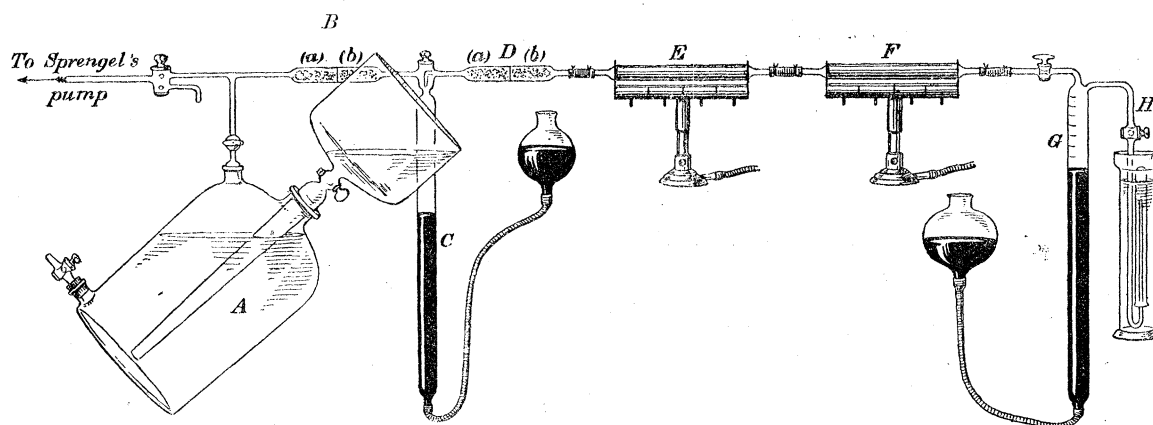
a result verified by experiment.

It is, of course, to be understood that these densities of nitrogen refer to atmospheric nitrogen, that is, to air from which oxygen, water vapour carbon dioxide, and ammonia have been removed.

ings, also heated to bright redness by means of a long-flame burner. H contained phosphoric anhydride, and I soda-lime. All joints were sealed, excepting those connecting the hard-glass tubes E and G to the tubes next them.

The gas-holder A having been filled with nitrogen, prepared by passing air over red-hot copper, and introduced at C, the gas was slowly passed through the system of tubes into the gas-holder B, and back again. The magnesium in the tube G having then ceased to absorb was quickly removed and replaced by a fresh tube. This tube was of course full of air, and before the tube G was heated, the air was carried back from B towards A by passing a little nitrogen from right to left. The oxygen in the air was removed by the metallic copper, and the nitrogen passed into the gas-holder A, to be returned in the opposite direction to B.

Fig. 4.



In the course of about ten days most of the nitrogen had been absorbed. The magnesium was not always completely exhausted; usually the nitride presented the appearance of a blackish-yellow mass, easily shaken out of the tube. It is needless to say that the tube was always somewhat attacked, becoming black with a coating of magnesium silicide. The nitride of magnesium, whether blackish or orange, if left for a few hours exposed to moist air, was completely converted into white, dusty hydroxide, and during exposure it gave off a strong odour of ammonia. If kept in a stoppered bottle, however, it was quite stable.

It was then necessary, in order to continue the absorption, to carry on operations on a smaller scale, with precautions to exclude atmospheric air as completely as possible. There was at this stage a residue of 1500 cub. centims.

The apparatus was therefore altered to that shown in fig. 4, so as to make it possible to withdraw all the gas out of the gas-holder A.

The left-hand exit led to the SPRENGEL'S pump; the compartment (a) of the drying-tube B was filled with soda-lime, and (b) with phosphoric anhydride. C is a

tube into which the gas could be drawn from the gas-holder A. The stop-cock, as shown, allows gas to pass through the horizontal tubes, and does not communicate with A; but a vertical groove allows it to be placed in communication either with the gas-holder, or with the apparatus to the right. The compartment (*a*) of the second drying-tube D contained soda-lime, and (*b*) phosphoric anhydride. The tube D communicated with a hard-glass tube E, heated over a long-flame burner; it was partly filled with metallic copper, and partly with copper oxide. This tube, as well as the tube F filled with magnesium turnings, was connected to the drying-tube with india-rubber. The gas then entered G, a graduated reservoir, and the arrangement H permitted the removal or introduction of gas from or into the apparatus. The gas was gradually transferred from the gas-holder to the tube C, and passed backwards and forwards over the red-hot magnesium until only about 200 cub. centims. were left. It was necessary to change the magnesium tube, which was made of smaller size than formerly, several times during the operation. This was done by turning out the long-flame burners and pumping off all gas in the horizontal tubes by means of the SPRENGEL'S pump. This gas was carefully collected. The magnesium tube was then exchanged for a fresh one, and after air had been exhausted from the apparatus, nitrogen was introduced from the reservoir. Any gas evolved from the magnesium (and apparently there was always a trace of hydrogen, either occluded by the magnesium, or produced by the action of aqueous vapour on the metal) was oxidised by the copper oxide. Had oxygen been present, it would have been absorbed by the metallic copper, but the copper preserved its red appearance without alteration, whereas a little copper oxide was reduced during the series of operations. The gas, which had been removed by pumping, was reintroduced at H, and the absorption continued.

The volume of the gas was thus, as has been said, reduced to about 200 cub. centims. It would have been advisable to take exact measurements, but, unfortunately, some of the original nitrogen had been lost through leakage; and a natural anxiety to see if there was any unknown gas led to pushing on operations as quickly as possible.

The density of the gas was next determined. The bulb or globe in which the gas was weighed was sealed to a two-way stop-cock, and the weight of distilled and air-free water filling it at 17.15° was 162.654 grms., corresponding to a capacity of 162.843 cub. centims. The shrinkage on removing air completely was 0.0212 cub. centim. Its weight, when empty, should therefore be increased by the weight of that volume of air, which may be taken as 0.000026 gm. This correction, however, is perhaps hardly worth applying in the present case.

The counterpoise was an exactly similar bulb of equal capacity, and weighing about 0.2 gm. heavier than the empty globe. The balance was a very sensitive one by OERTLING, which easily registered one-tenth of a milligram. By the process of swinging, one-hundredth of a milligram, could be determined with fair accuracy.

In weighing the empty globe, 0.2 gm. was placed on the same pan as that which

hung from the end of the beam to which it was suspended, and the final weight was adjusted by means of a rider, or by small weights on the other pan. This process practically leads to weighing by substitution of gas for weights. The bulb was always handled with gloves, to avoid moisture or grease from the fingers.

Three experiments, of which it is unnecessary to give details, were made to test the degree of accuracy with which a gas could be weighed, the gas being dried air, freed from carbon dioxide. The mean result gave for the weight of one litre of air at 0° and 760 millims. pressure, 1.2935 gm. REGNAULT found 1.29340, a correction having been applied by CRAFTS to allow for the estimated alteration of volume caused by the contraction of his vacuous bulb. The mean result of determinations by several observers is 1.29347; while one of us found 1.29327.

The globe was then filled with the carefully dried gas.

Temperature, 18.80° .	Pressure, 759.3 millims.	
Weight of 162.843 cub. centims. of gas		0.21897 gm.
Weight of 1 litre gas at 0° and 760 millims.		1.4386 „
Density, that of air compared with O, = 16, being 14.476	16.100	grms.

It is evident from these numbers that the dense constituent of the air was being concentrated. As a check, the bulb was pumped empty and again weighed; its weight was 0.21903 gm. This makes the density 16.105.

It appeared advisable to continue to absorb nitrogen from this gas. The first tube of magnesium removed a considerable quantity of gas; the nitride was converted into ammonium chloride, and the sample contained 66.30 per cent. of chlorine, showing, as has before been remarked, that if any of the heavier constituent of the atmosphere had been absorbed, it formed no basic compound with hydrogen. The second tube of magnesium was hardly attacked; most of the magnesium had melted, and formed a layer at the lower part of the tube. That which was still left in the body of the tube was black on the surface, but had evidently not been much attacked. The ammonium chloride which it yielded weighed only 0.0035 gm.

The density of the remaining gas was then determined. But as its volume was only a little over 100 cub. centims., the bulb, the capacity of which was 162 cub. centims., had to be filled at reduced pressure. This was easily done by replacing the pear-shaped reservoir of the mercury gas-holder by a straight tube, and noting the level of the mercury in the gas-holder and in the tube which served as a mercury reservoir against a graduated mirror-scale by help of a cathetometer at the moment of closing the stop-cock of the density bulb.

The details of the experiment are these:—

Temperature, 19.12° C.	Barometric pressure, 749.8 millims. (corr.).
Difference read on gas-holder and tube, 225.25 millims. (corr.).	
Actual pressure, 524.55 millims.	

Weight of 162·843 cub. centims. of gas	0·17913	grm.
Weight of 1 litre at 0° and 760 millims. pressure	1·7054	„
Density	19·086	grms.

This gas is accordingly at least 19 times as heavy as hydrogen.

A portion of the gas was then mixed with oxygen, and submitted to a rapid discharge of sparks for four hours in presence of caustic potash. It contracted, and on absorbing the excess of oxygen with pyrogallate of potassium the contraction amounted to 15·4 per cent. of the original volume. The question then arises, if the gas contain 15·4 per cent. of nitrogen, of density 14·014, and 84·6 per cent. of other gas, and if the density of the mixture were 19·086, what would be the density of the other gas? Calculation leads to the number 20·0.

A vacuum-tube was filled with a specimen of the gas of density 19·086, and it could not be doubted that it contained nitrogen, the bands of which were distinctly visible. It was probable, therefore, that the true density of the pure gas lay not far from 20 times that of hydrogen. At the same time many lines were seen which could not be recognized as belonging to the spectrum of any known substance.

Such were the preliminary experiments made with the aid of magnesium to separate from atmospheric nitrogen its dense constituent. The methods adopted in preparing large quantities will be subsequently described.

6. *Proof of the Presence of Argon in Air, by means of Atmolysis.*

It has already (§ 2) been suggested that if “atmospheric nitrogen” contains two gases of different densities, it should be possible to obtain direct evidence of the fact by the method of atmolysis. The present section contains an account of carefully conducted experiments directed to this end.

The atmolyser was prepared (after GRAHAM) by combining a number of “church-warden” tobacco pipes. At first twelve pipes were used in three groups, each group including four pipes connected in series. The three groups were then connected in parallel, and placed in a large glass tube closed in such a way that a partial vacuum could be maintained in the space outside the pipes by a water-pump. One end of the combination of pipes was open to the atmosphere, or rather was connected with the interior of an open bottle containing sticks of caustic alkali, the object being mainly to dry the air. The other end of the combination was connected to a bottle aspirator, initially full of water, and so arranged as to draw about two per cent. of the air which entered the other end of the pipes. The gas collected was thus a very small proportion of that which leaked through the pores of the pipes, and should be relatively rich in the heavier constituents of the atmosphere. The flow of water from the aspirator could not be maintained very constant, but the rate of two per cent. was never much exceeded. The necessary four litres took about sixteen hours to collect.