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Argon, a New Constituent of the Atmosphere

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VI. *Argon, a New Constituent of the Atmosphere.*

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> "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 CO_2 and H_2O, 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.

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* 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, $AgNO_3 : Ag = 1·57490 : 1$, 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 31	·52395
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

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* 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

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[*] "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 alkalies, 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 decompound 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 12½ 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

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* '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

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* '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

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

[†] Ouvrard, 'Comptes Rendus,' 114, 120.

[‡] Ouvrard, '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 MALLET.* 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.

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

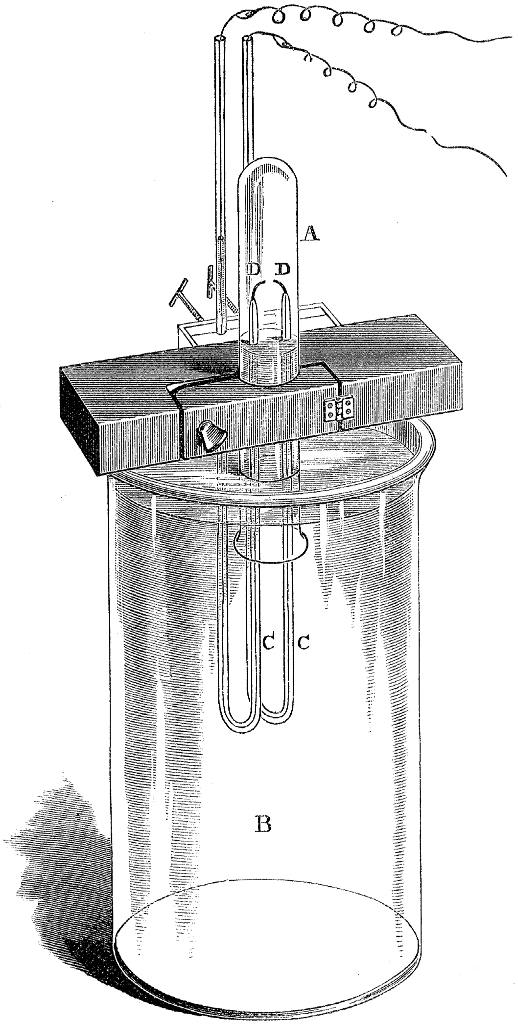
[†] 'Annalen der Chemie u. Pharmacie,' 195, 373.

[‡] 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, 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.

Fig. 1.



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*

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* 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,

$$W = \frac{A}{2V_2}(V + V_2)(V - V_2) = A(V - V_2)$$

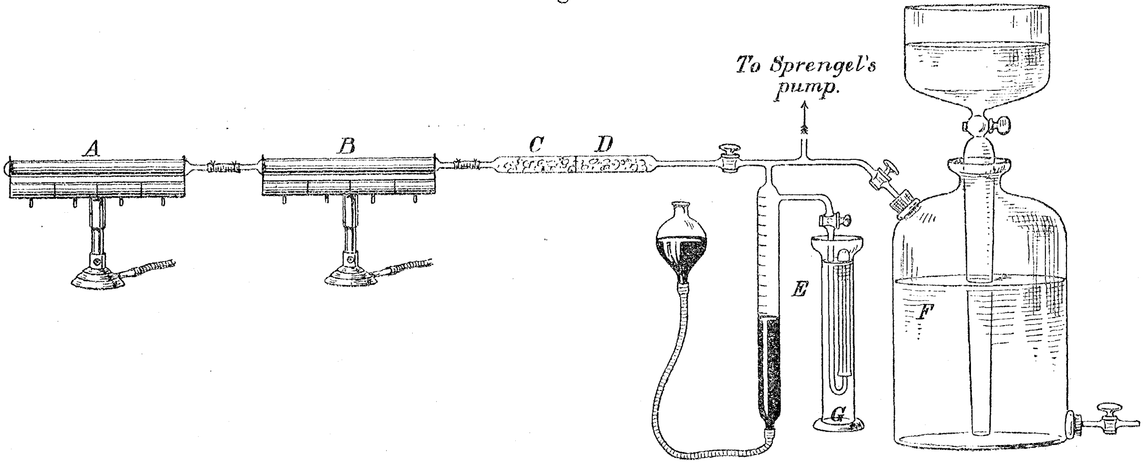
$$= 2{\cdot}4 \times 2{\cdot}5 = 6{\cdot}0 \text{ approximately.}$$

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 :—

	grm.
(*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.

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* 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

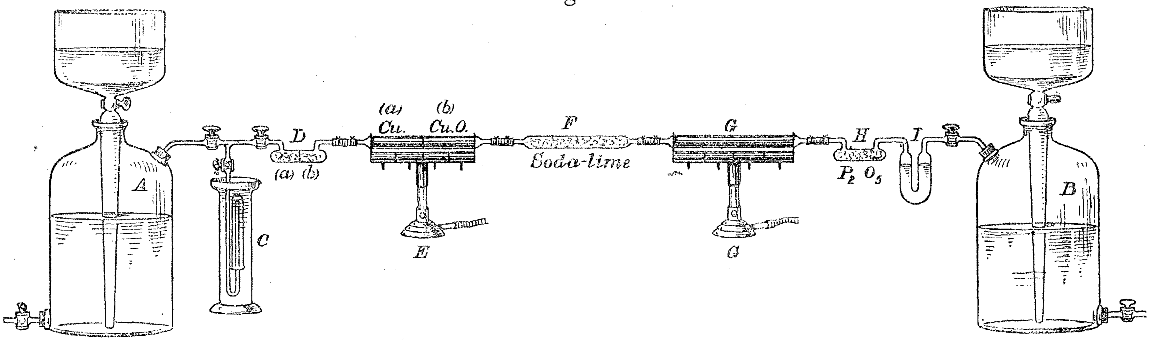
REGNAULT'S numbers have an approximate correction applied to them by CRAFTS. The mean of these

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-

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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 ,,

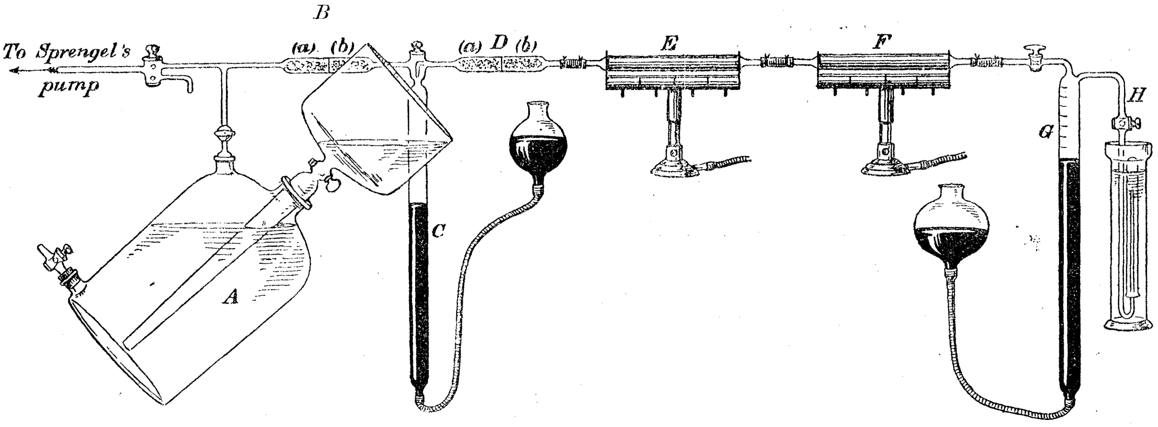
a result verified by experiment.

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 grm. 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 grm. heavier than the empty globe. The balance was a very sensitive one by OERTLING, which easily registered one-tenth of a milligrm. By the process of swinging, one-hundredth of a milligrm. could be determined with fair accuracy.

In weighing the empty globe, 0·2 grm. 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 grm. 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	grm.
Weight of 1 litre gas at 0° and 760 millims.	1·4386	,,
Density, that of air compared with $O_2 = 16$, 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 grm. 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 grm.

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 cathetomer 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 "churchwarden" 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.

The air thus obtained was treated exactly as ordinary air had been treated in determinations of the density of atmospheric nitrogen. Oxygen was removed by red-hot copper followed by cupric oxide, ammonia by sulphuric acid, carbonic anhydride and moisture by potash and phosphoric anhydride.

The following are the results :—

Globe empty July 10, 14	2·81789
Globe full September 15 (twelve pipes)	·50286
Weight of gas	2·31503
Ordinary atmospheric nitrogen	2·31016
Difference	+ ·00487

Globe empty September 17	2·81345
Globe full September 18 (twelve pipes)	·50191
Weight of gas	2·31154
Ordinary atmospheric nitrogen	2·31016
Difference	+ ·00138

Globe empty September 21	2·82320
Globe full September 20 (twelve pipes)	·51031
Weight of gas	2·31289
Ordinary atmospheric nitrogen	2·31016
Difference	+ ·00273

Globe empty September 21, October 30	2·82306
Globe full September 22 (twelve pipes)	·51140
Weight of gas	2·31166
Ordinary atmospheric nitrogen	2·31016
Difference	+ ·00150

The mean excess of the four determinations is ·00262 gram., or if we omit the first, which depended upon a vacuum weighing of two months old, ·00187 gram.

The gas from prepared air was thus in every case denser than from unprepared air, and to an extent much beyond the possible errors of experiment. The excess was, however, less than had been expected, and it was thought that the arrangement of the pipes could be improved. The final delivery of gas from each of the groups in parallel being so small in comparison with the whole streams concerned, it seemed possible that each group was not contributing its proper share, and even that there might be a flow in the wrong direction at the delivery end of one or two of them. To meet this objection, the arrangement in parallel had to be abandoned, and for the remaining experiments eight pipes were connected in simple series. The porous surface in operation was thus reduced, but this was partly compensated for by an improved vacuum. Two experiments were made under the new conditions:—

Globe empty, October 30, November 5	2·82313
Globe full, November 3 (eight pipes)	·50930
Weight of gas	2·31383
Ordinary atmospheric nitrogen	2·31016
Difference	+ ·00367

Globe empty, November 5, 8	2·82355
Globe full, November 6 (eight pipes)	·51011
Weight of gas	2·31344
Ordinary atmospheric nitrogen	2·31016
Difference	+ ·00328

The excess being larger than before is doubtless due to the greater efficiency of the atmolysing apparatus. It should be mentioned that the above recorded experiments include all that have been tried, and the conclusion seems inevitable that "atmospheric nitrogen" is a mixture and not a simple body.

It was hoped that the concentration of the heavier constituent would be sufficient to facilitate its preparation in a pure state by the use of prepared air in substitution for ordinary air in the oxygen apparatus. The advance of $3\frac{1}{2}$ mg. on the 11 mg., by which atmospheric nitrogen is heavier than chemical nitrogen, is indeed not to be despised, and the use of prepared air would be convenient if the diffusion apparatus could be set up on a large scale and be made thoroughly self-acting.

7. *Negative Experiments to Prove that Argon is not derived from Nitrogen or from Chemical Sources.*

Although the evidence of the existence of argon in the atmosphere, derived from the comparison of densities of atmospheric and chemical nitrogen and from the diffusion experiments (§ 6), appeared overwhelming, we have thought it undesirable to shrink from any labour that would tend to complete the verification. With this object in view, an experiment was undertaken and carried to a conclusion on November 13, in which 3 litres of chemical nitrogen, prepared from ammonium nitrite, were treated with oxygen in precisely the manner in which atmospheric nitrogen had been found to yield a residue of argon. In the course of operations an accident occurred, by which no gas could have been lost, but of such a nature that from 100 to 200 cub. centims. of air must have entered the working vessel. The gas remaining at the close of the large scale operations was worked up as usual with battery and coil until the spectrum showed only slight traces of the nitrogen lines. When cold, the residue measured 4 cub. centims. This was transferred, and after treatment with alkaline pyrogallate to remove oxygen, measured 3·3 cub. centims. If atmospheric nitrogen had been employed, the final residue should have been about 30 cub. centims. Of the 3·3 cub. centims. actually left, a part is accounted for by the accident alluded to, and the result of the experiment is to show that argon is not formed by sparking a mixture of oxygen and chemical nitrogen.

In a second experiment of the same kind 5660 cub. centims. of nitrogen from ammonium nitrite were treated with oxygen in the large apparatus (fig. 7, § 8). The final residue was 3·5 cub. centims.; and as evidenced by the spectrum, it consisted mainly of argon.

The source of the residual argon is to be found in the water used for the manipulation of the large quantities of gas (6 litres of nitrogen and 11 litres of oxygen) employed. Unfortunately the gases had been collected by allowing them to bubble up into aspirators charged with ordinary water, and they were displaced by ordinary water. In order to obtain information with respect to the contamination that may be acquired in this way, a parallel experiment was tried with carbonic anhydride. Eleven litres of the gas, prepared from marble and hydrochloric acid with ordinary precautions for the exclusion of air, were collected exactly as oxygen was commonly collected. It was then transferred by displacement with water to a gas pipette charged with a solution containing 100 grms. of caustic soda. The residue which refused absorption measured as much as 110 cub. centims. In another experiment where the water employed had been partially de-aerated, the residue left amounted to 71 cub. centims., of which 26 cub. centims. were oxygen. The quantities of dissolved gases thus extracted from water during the collection of oxygen and nitrogen suffice to explain the residual argon of the negative experiments.

It may perhaps be objected that the impurity was contained in the carbonic anhydride itself as it issued from the generating vessel, and was not derived from the water in the gas-holder; and indeed there seems to be a general impression that it is difficult to obtain carbonic anhydride in a state of purity. To test this question, 18 litres of the gas, made in the same generator and from the same materials, were passed directly into the absorption pipette. Under these conditions, the residue was only $6\frac{1}{2}$ cub. centims., corresponding to 4 cub. centims. from 11 litres. The quantity of gas employed was determined by decomposing the resulting sodium carbonate with hydrochloric acid, allowance being made for a little carbonic anhydride contained in the soda as taken from the stock bottle. It will be seen that there is no difficulty in reducing the impurity to $\frac{1}{3000}$th, even when india-rubber connections are freely used, and no extraordinary precautions are taken. The large amount of impurity found in the gas when collected over water must therefore have been extracted from the water.

A similar set of experiments was carried out with magnesium. The nitrogen, of which three litres were used, was prepared by the action of bleaching-powder on ammonium chloride. It was circulated in the usual apparatus over red-hot magnesium, until its volume had been reduced to about 100 cub. centims. An equal volume of hydrogen was then added, owing to the impossibility of circulating a vacuum. The circulation then proceeded until all absorption had apparently stopped. The remaining gas was then passed over red-hot copper oxide into the SPRENGEL'S pump, and collected. As it appeared still to contain hydrogen, which had escaped oxidation, owing to its great rarefaction, it was passed over copper oxide for a second and a third time. As there was still a residue, measuring 12·5 cub. centims., the gas was left in contact with red-hot magnesium for several hours, and then pumped out; its volume was then 4·5 cub. centims. Absorption was, however, still proceeding, when the experiment terminated, for at a low pressure, the rate is exceedingly slow. This gas, after being sparked with oxygen contracted to 3·0 cub. centims., and on examination was seen to consist mainly of argon. The amount of residue obtainable from three litres of atmospheric nitrogen should have amounted to a large multiple of this quantity.

In another experiment, 15 litres of nitrogen prepared from a mixture of ammonium chloride and sodium nitrite by warming in a flask (some nitrogen having first been drawn off by a vacuum-pump, in order to expel all air from the flask and from the contained liquid) were collected over water in a large gas-holder. The nitrogen was not bubbled through the water, but was admitted from above, while the water escaped below. This nitrogen was absorbed by red-hot magnesium, contained in tubes heated in a combustion-furnace. The unabsorbed gas was circulated over red-hot magnesium in a special small apparatus, by which its volume was reduced to 15 cub. centims. As it was impracticable further to reduce the volume by means of magnesium, the residual 15 cub. centims. were transferred to a tube, mixed with oxygen, and submitted to sparking over caustic soda. The residue after absorption of oxygen, which undoubtedly consisted of pure argon, amounted to 3·5 cub. centims. This is one-fortieth of the quantity which would have been obtained from atmospheric nitrogen, and its presence can be accounted for, we venture to think, first from the water in the gas-holder, which had not been freed from dissolved gas by boiling *in vacuo* (it has already been shown that a considerable gain may ensue from this source), and second, from leakage of air which accidentally took place, owing to the breaking of a tube. The leakage may have amounted to 200 cub. centims., but it could not be accurately ascertained. Quantitative negative experiments of this nature are exceedingly difficult, and require a long time to carry them to a successful conclusion.

8. *Separation of Argon on a Large Scale.*

To separate nitrogen from "atmospheric nitrogen" on a large scale, by help of magnesium, several devices were tried. It is not necessary to describe them all in detail. Suffice it to say that an attempt was made to cause a store of "atmospheric nitrogen" to circulate by means of a fan, driven by a water-motor. The difficulty encountered here was leakage at the bearing of the fan, and the introduced air produced a cake which blocked the tube on coming into contact with the magnesium. It might have been possible to remove oxygen by metallic copper; but instead of thus complicating the apparatus, a water-injector was made use of to induce circulation. Here also it is unnecessary to enter into details. For, though the plan worked well, and although about 120 litres of "atmospheric nitrogen" were absorbed, the yield of argon was not large, about 600 cub. centims. having been collected. This loss was subsequently discovered to be due partially, at least, to the relatively high solubility of argon in water. In order to propel the gas over magnesium, through a long combustion-tube packed with turnings, a considerable water-pressure, involving a large flow of water, was necessary. The gas was brought into intimate contact with this water, and presuming that several thousand litres of water ran through the injector, it is obvious that a not inconsiderable amount of argon must have been dissolved. Its proportion was increasing at each circulation, and consequently its partial pressure also increased. Hence, towards the end of the operation, at least, there is every reason to believe that a serious loss had occurred.

It was next attempted to pass "atmospheric nitrogen" from a gas-holder first through a combustion tube of the usual length packed with metallic copper reduced from the oxide; then through a small U-tube containing a little water, which was intended as an index of the rate of flow; the gas was then dried by passage through tubes filled with soda-lime and phosphoric anhydride; and it next passed through a long iron tube (gas-pipe) packed with magnesium turnings, and heated to bright redness in a second combustion-furnace.

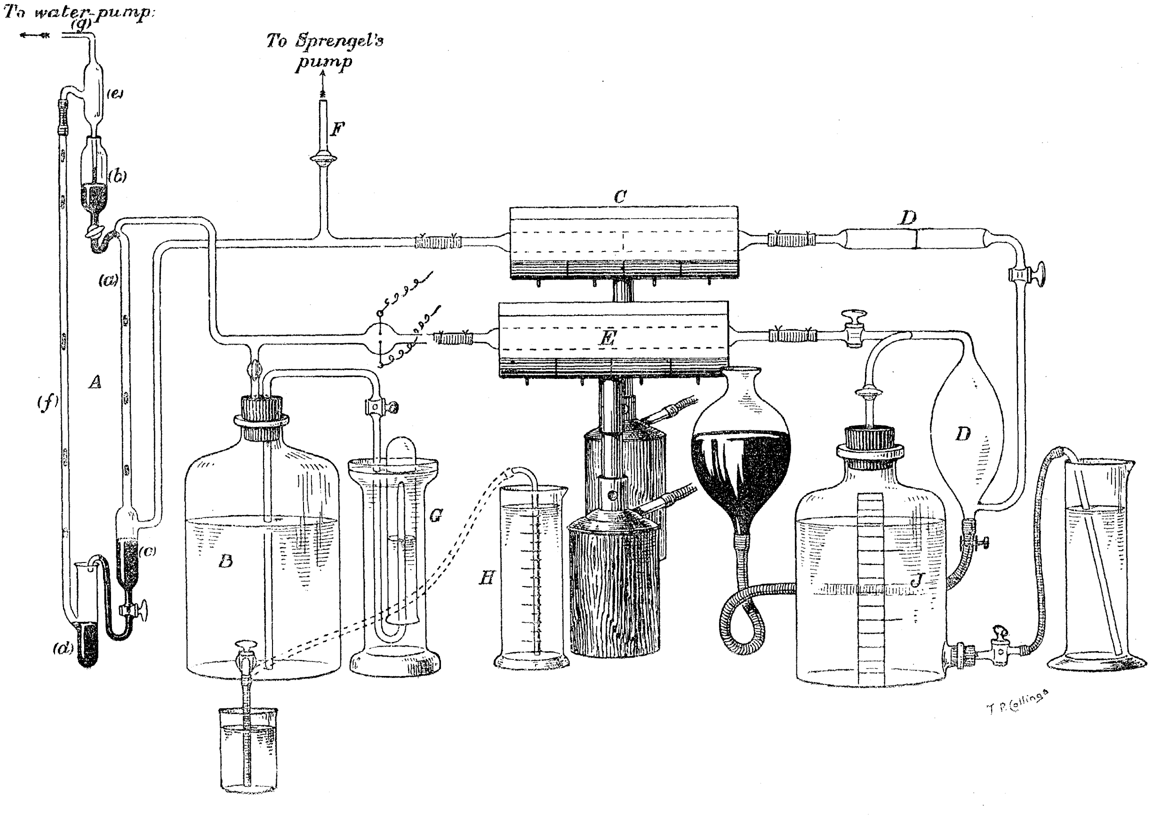
After the iron tube followed a second small U-tube containing water, intended to indicate the rate at which the argon escaped into a small gas-holder placed to receive it. The nitrogen was absorbed rapidly, and argon entered the small gas-holder. But there was reason to suspect that the iron tube is permeable by argon at a red heat. The first tube-full allowed very little argon to pass. After it had been removed and replaced by a second, the same thing was noticed. The first tube was difficult to clean; the nitride of magnesium forms a cake on the interior of the tube, and it was very difficult to remove it; moreover this rendered the filling of the tube very troublesome, inasmuch as its interior was so rough that the magnesium turnings could only with difficulty be forced down. However, the permeability to argon, if such be the case, appeared to have decreased. The iron tube was coated internally with a skin of magnesium nitride, which appeared to diminish its permeability to argon.

After all the magnesium in the tube had been converted into nitride (and this was easily known, because a bright glow proceeded gradually from one end of the tube to the other) the argon remaining in the iron tube was "washed" out by a current of nitrogen; so that after a number of operations, the small gas-holder contained a mixture of argon with a considerable quantity of nitrogen.

On the whole, the use of iron tubes is not to be recommended, owing to the difficulty in cleaning them, and the possible loss through their permeability to argon. There is no such risk of loss with glass tubes, but each operation requires a new tube, and the cost of the glass is considerable if much nitrogen is to be absorbed. Tubes of porcelain were tried; but the glaze in the interior is destroyed by the action of the red-hot magnesium, and the tubes crack on cooling.

By these processes 157 litres of "atmospheric nitrogen" were reduced in volume to about 2·5 litres in all of a mixture of nitrogen and argon. This mixture was afterwards circulated over red-hot magnesium, in order to remove the last portion of nitrogen.

Fig. 5.



As the apparatus employed for this purpose proved very convenient, a full description of its construction is here given. A diagram is shown in fig. 5, which sufficiently explains the arrangement of the apparatus. A is the circulator. It consists of a sort of SPRENGEL's pump (a) to which a supply of mercury is admitted from a small reservoir (*b*). This mercury is delivered into a gas-separator (*c*), and the mercury overflows into the reservoir (*d*). When its level rises, so that it blocks the tube (*f*), it ascends in pellets or pistons into (*e*), a reservoir which is connected through (*g*) with a water-pump. The mercury falls into (*b*), and again passes down the SPRENGEL tube (*a*). No attention is, therefore, required, for the apparatus works quite automatically. This form of apparatus was employed several years ago by Dr. COLLIE.

The gas is drawn from the gas-holder B, and passes through a tube C, which is heated to redness by a long-flame burner, and which contains in one half metallic copper, and in the other half copper oxide. This precaution is taken in order to remove any oxygen which may possibly be present, and also any hydrogen or hydrocarbon. In practice, it was never found that the copper became oxidised, or the oxide reduced. It is, however, useful to guard against any possible contamination. The gas next traversed a drying-tube D, the anterior portion containing ignited soda-lime, and the posterior portion phosphoric anhydride. From this it passed a reservoir, D′, from which it could be transferred, when all absorption had ceased, into the small gas-holder. It then passed through E, a piece of combustion-tube, drawn out at both ends, filled with magnesium turnings, and heated by a long-flame burner to redness. Passing through a small bulb, provided with electrodes, it again entered the fall tube.

After the magnesium tube E had done its work, the stop-cocks were all closed, and the gas was turned down, so that the burners might cool. The mixture of argon and nitrogen remaining in the system of tubes was pumped out by a SPRENGEL'S pump through F, collected in a large test-tube, and reintroduced into the gas-holder B through the side-tube G, which requires no description. The magnesium tube was then replaced by a fresh one; the system of tubes was exhausted of air; argon and nitrogen were admitted from the gas-holder B; the copper-oxide tube and the magnesium tube were again heated; and the operation was repeated until absorption ceased. It was easy to decide when this point had been reached, by making use of the graduated cylinder H, from which water entered the gas-holder B. It was found advisable to keep all the water employed in these operations, for it had become saturated with argon. If gas was withdrawn from the gas-holder, its place was taken by this saturated water.

The absorption of nitrogen proceeds very slowly towards the end of the operation, and the diminution in volume of the gas is not greater than 4 or 5 cub. centims. per hour. It is, therefore, somewhat difficult to judge of the end-point, as will be seen when experiments on the density of this gas are described. The magnesium tube, towards the end of the operations, was made so hot that the metal was melted in the lower part of the tube, and sublimed in the upper part. The argon and residual nitrogen had, therefore, been thoroughly mixed with gaseous magnesium during its passage through the tube E.

To avoid possible contamination with air in the SPRENGEL'S pump, the last portion of gas collected from the system of tubes was not re-admitted to the gas-holder B, but was separately stored.

The crude argon was collected in two operations. First, the quantity made by absorption by magnesium in glass tubes with the water-pump circulator was purified. Later, after a second supply had been prepared by absorption in iron tubes, the mixture of argon and nitrogen was united with the first quantity and circulated by means of the mercury circulator, in the gas-holder B. Attention will be drawn to the particular sample of gas employed in describing further experiments made with the argon.

By means of magnesium, about 7 litres of nitrogen can be absorbed in an hour. The changing of the tubes of magnesium, however, takes some time; consequently, the largest amount absorbed in one day was nearly 30 litres.

At a later date a quantitative experiment was carried out on a large scale, the amount of argon from 100 litres of "atmospheric" nitrogen, measured at 20°, having been absorbed by magnesium, and the resulting argon measured at 12°. During the process of absorbing nitrogen in the combustion-furnace, however, one tube cracked, and it is estimated that about 4 litres of nitrogen escaped before the crack was noticed. With this deduction, and assuming that the nitrogen had been measured at 12°, 93·4 litres of atmospheric nitrogen were taken. The magnesium required for absorption weighed 409 grms. The amount required by theory should have been 285 grms.; but it must be remembered that in many cases the magnesium was by no means wholly converted into nitride. The first operation yielded about 3 litres of a mixture of nitrogen and argon, which was purified in the circulating apparatus. The total residue, after absorption of the nitrogen, amounted to 921 cub. centims. The yield is therefore 0·986 per cent.

At first no doubt the nitrogen gains a little argon from the water over which it stands. But, later, when the argon forms the greater portion of the gaseous mixture, its solubility in water must materially decrease its volume. It is difficult to estimate the loss from this cause. The gas-holder, from which the final circulation took place, held three litres of water. Taking the solubility of argon as 4 per cent., this would mean a loss of about 120 cub. centims. If this is not an over-estimate, the yield of argon would be increased to 1040 cub. centims., or 1·11 per cent. The truth probably lies between these two estimates.

It may be concluded, with probability, that the argon forms approximately 1 per cent. of the "atmospheric" nitrogen.

The principal objection to the oxygen method of isolating argon, as hitherto described, is the extreme slowness of the operation. An absorption of 30 cub. centims. of mixed gas means the removal of but 12 cub. centims. of nitrogen. At this rate 8 hours are required for the isolation of 1 cub. centim. of argon, supposed to be present in the proportion of 1 per cent.

In extending the scale of operations we had the great advantage of the advice of

Mr. CROOKES, who a short time ago called attention to the flame rising from platinum terminals, which convey a high tension alternating electric discharge, and pointed out its dependence upon combustion of the nitrogen and oxygen of the air.* Mr. CROOKES was kind enough to arrange an impromptu demonstration at his own house with a small alternating current plant, in which it appeared that the absorption of mixed gas was at the rate of 500 cub. centims. per hour, or nearly 20 times as fast as with the battery. The arrangement is similar to that first described by SPOTTISWOODE.† The primary of a RUHMKORFF coil is connected directly with the alternator, no break or condenser being required; so that, in fact, the coil acts simply as a high potential transformer. When the arc is established the platinum terminals may be separated much beyond the initial striking distance.

The plant with which the large scale operations have been made consists of a DE MERITENS alternator, kindly lent by Professor J. J. THOMSON, and a gas engine. As transformer, one of SWINBURNE'S hedgehog pattern has been employed with success, but the ratio of transformation (24 : 1) is scarcely sufficient. A higher potential, although, perhaps, not more efficient, is more convenient. The striking distance is greater, and the arc is not so liable to go out. Accordingly most of the work to be described has been performed with transformers of the RUHMKORFF type.

The apparatus has been varied greatly, and it cannot be regarded as having even yet assumed a final form. But it will give a sufficient idea of the method if we describe an experiment in which a tolerably good account was kept of the air and oxygen employed. The working vessel was a glass flask, A (fig. 6), of about 1500 cub. centims. capacity, and stood, neck downwards, over a large jar of alkali, B. As in the small scale experiments, the leading-in wires were insulated by glass tubes, DD, suitably bent and carried through the liquid up the neck. For the greater part of the length iron wires were employed, but the internal extremities, EE, were of platinum, doubled upon itself at the terminals from which the discharge escaped. The glass protecting tubes must be carried up for some distance above the internal level of the liquid, but it is desirable that the arc itself should not be much raised above that level. A general idea of the disposition of the electrodes will be obtained from fig. 6. To ensure gas tightness the bends were occupied by mercury. A tube, C, for the supply or withdrawal of gas was carried in the same way through the neck.

The RUHMKORFF employed in this operation was one of medium size. When the mixture was rightly proportioned and the arc of full length, the rate of absorption was about 700 cub. centims. per hour. A good deal of time is lost in starting, for, especially when there is soda on the platinums, the arc is liable to go out if lengthened prematurely. After seven days the total quantity of air let in amounted to 7925 cub. centims., and of oxygen (prepared from chlorate of potash) 9137 cub. centims. On

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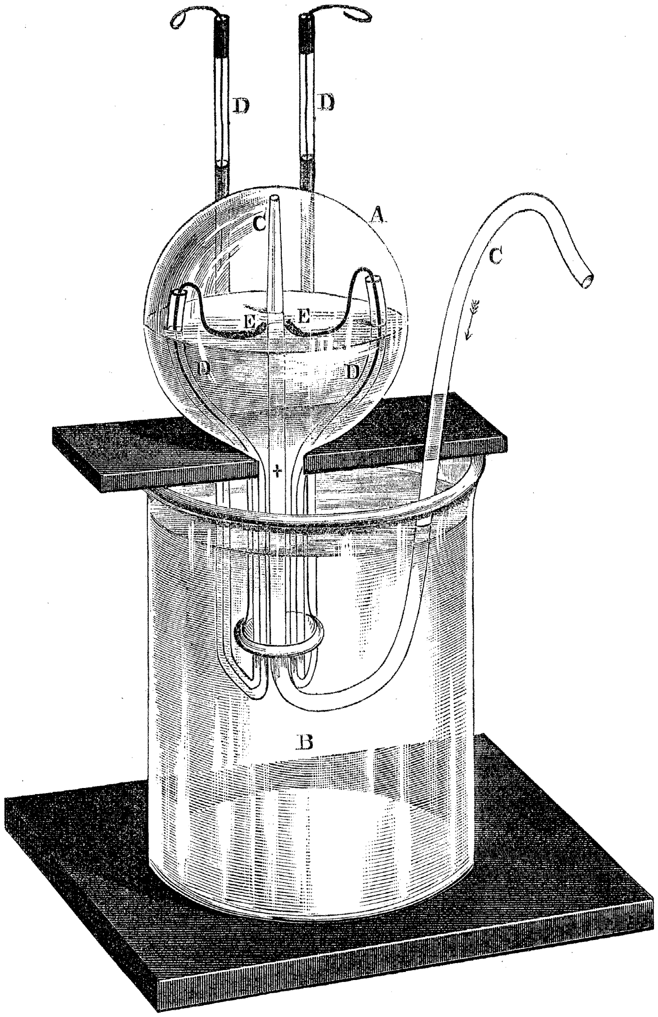
* 'Chemical News,' vol. 65, p. 301, 1892.

† "A Mode of Exciting an Induction-coil." 'Phil. Mag.,' vol. 8, p. 390, 1879.

the eighth and ninth days oxygen alone was added, of which about 500 cub. centims. was consumed, while there remained about 700 cub. centims in the flask. Hence the proportion in which the air and oxygen combined was as 70 : 96. On the eighth day there was about three hours' work, and the absorption slackened off to about one quarter of the previous rate. On the ninth day (September 8) the rate fell off still more, and after three hours' work became very slow. The progress towards removal of nitrogen was examined from time to time with the spectroscope, the points being approximated and connected with a small Leyden jar. At this stage the yellow nitrogen line was faint, but plainly visible. After about four hours' more work, the yellow line had disappeared, and for two hours there had been no visible contraction. It will be seen that the removal of the last part of the nitrogen was very slow, mainly on account of the large excess of oxygen present.

Fig. 6.



The final treatment of the residual 700 cub. centims. of gas was on the model of the small scale operations already described (§ 4). By means of a pipette the gas was gradually transferred to a large test-tube standing over alkali. Under the influence of sparks (from battery and coil) passing all the while, the superfluous oxygen was consumed with hydrogen fed in slowly from a voltameter. If the nitrogen had been completely removed, and if there were no unknown ingredient in the atmosphere, the volume under this treatment should have diminished without limit. But the contraction stopped at a volume of 65 cub. centims., and the volume was taken backwards and forwards through this as a minimum by alternate treatment with oxygen and hydrogen added in small quantities, with prolonged intervals of sparking. Whether the oxygen or the hydrogen were in excess could be determined at any moment by a glance at the spectrum. At the minimum volume the gas was certainly not hydrogen or oxygen. Was it nitrogen? On this point the testimony of the spectroscope was equally decisive. No trace of the yellow nitrogen line could be seen even with a wide slit and under the most favourable conditions.

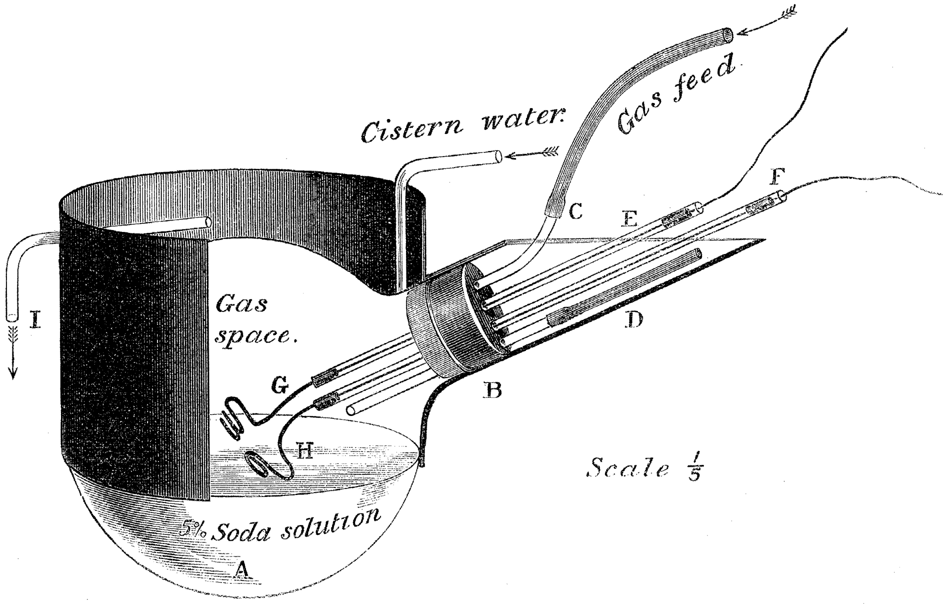
When the gas stood for some days over water the nitrogen line again asserted itself, and many hours of sparking with a little oxygen were required again to get rid of it. As it was important to know what proportions of nitrogen could be made visible in this way, a little air was added to gas that had been sparked for some time subsequently to the disappearance of nitrogen in its spectrum. It was found that about 1½ per cent. was clearly, and about 3 per cent. was conspicuously, visible. About the same numbers apply to the visibility of nitrogen in oxygen when sparked under these conditions, that is, at atmospheric pressure, and with a jar in connection with the secondary terminals.

When we attempt to increase the rate of absorption by the use of a more powerful electric arc, further experimental difficulties present themselves. In the arrangement already described, giving an absorption of 700 cub. centims. per hour, the upper part of the flask becomes very hot. With a more powerful arc the heat rises to such a point that the flask is filled with steam and the operation comes to a standstill.

It is necessary to keep the vessel cool by either the external or internal application of liquid to the upper surface upon which the hot gases from the arc impinge. One way of effecting this is to cause a small fountain of alkali to impinge on the top of the flask, so as to wash the whole of the upper surface. This plan is very effective, but it is open to the objection that a break-down would be disastrous, and it would involve special arrangements to avoid losing the argon by solution in the large quantity of alkali required. It is simpler in many respects to keep the vessel cool by immersing it in a large body of water, and the inverted flask arrangement (fig. 6) has been applied in this manner. But, on the whole, it appears to be preferable to limit the application of the cooling water to the upper part of the external surface, building up for this purpose a suitable wall of sheet lead cemented round the glass. The most convenient apparatus for large-scale operations that has hitherto been tried is shown in the accompanying figure (fig. 7).

The vessel A is a large globe of about 6 litres capacity, intended for demonstrating the combustion of phosphorus in oxygen gas, and stands in an inclined position. It is about half filled with a solution of caustic soda. The neck is fitted with a rubber stopper, B, provided with four perforations. Two of these are fitted with tubes, C, D, suitable for the supply or withdrawal of gas or liquid. The other two allow the passage of the stout glass tubes, E, F, which contain the electrodes. For greater security against leakage, the interior of these tubes is charged with water, held in place by small corks, and the outer ends are cemented up. The electrodes are formed of stout iron wires terminated by thick platinums, G, H, triply folded together, and welded at the ends. The lead walls required to enclose the cooling water are partially shown at I. For greater security the india-rubber cork is also drowned in water, held in place with the aid of sheet-lead. The lower part of the globe is occupied by about 3 litres of a 5 per cent. solution of caustic soda, the solution rising to within about half-an-inch of the platinum terminals. With this apparatus an absorption of 3 litres of mixed gas per hour can be attained,—about 3000 times the rate at which CAVENDISH could work.

Fig. 7.



When it is desired to stop operations, the feed of air (or of chemical nitrogen in blank experiments) is cut off, oxygen alone being supplied as long as any visible absorption occurs. Thus at the close the gas space is occupied by argon and oxygen with such nitrogen as cannot readily be taken up in a condition of so great dilution.

The oxygen, being too much for convenient treatment with hydrogen, was usually absorbed with copper and ammonia, and the residual gas was then worked over again as already described in an apparatus constructed upon a smaller scale.

It is worthy of notice that with the removal of the nitrogen, the arc-discharge from the dynamo changes greatly in appearance, bridging over more directly and in a narrower band from one platinum to the other, and assuming a beautiful sky-blue colour, instead of the greenish hue apparent so long as oxidation of nitrogen is in progress.

In all the large-scale experiments, an attempt was made to keep a reckoning of the air and oxygen employed, in the hope of obtaining data as to the proportional volume of argon in air, but various accidents too often interfered. In one successful experiment (January, 1895), specially undertaken for the sake of measurement, the total air employed was 9250 cub. centims., and the oxygen consumed, manipulated with the aid of partially de-aerated water, amounted to 10,820 cub. centims. The oxygen contained in the air would be 1942 cub. centims.; so that the quantities of "atmospheric nitrogen" and of total oxygen which enter into combination would be 7308 cub. centims., and 12,762 cub. centims. respectively. This corresponds to $N + 1{\cdot}75O$—the oxygen being decidedly in excess of the proportion required to form nitrous acid—$2HNO_2$, or $H_2O + N_2 + 3O$. The argon ultimately found on absorption of the excess of oxygen was 75·0 cub. centims., reduced to conditions similar to those under which the air was measured, or a little more than 1 per cent. of the "atmospheric nitrogen" used. It is probable, however, that some of the argon was lost by solution during the protracted operations required in order to get quit of the last traces of nitrogen.

[In recent operations at the Royal Institution, where a public supply of alternating current at 100 volts is available, the scale of the apparatus has been still further increased.

The capacity of the working vessel is 20 litres, of which about one half is occupied by a strong solution of caustic soda. The platinum terminals are very massive, and the flame rising from them is prevented from impinging directly upon the glass by a plate of platinum held over it and supported by a wire which passes through the rubber cork. In the electrical arrangements we have had the advantage of Mr. Swinburne's advice. The transformers are two of the "hedgehog" pattern, the thick wires being connected in parallel and the thin wires in series. In order to control the current taken when the arc is short or the platinums actually in contact, a choking-coil, provided with a movable core of fine iron wires, is inserted in the thick wire circuit. In normal working the current taken from the mains is about 22 amperes, so that some 2½ h. p. is consumed. At the same time the actual voltage at the platinum terminals is 1500. When the discharge ceases, the voltage at the platinum rises to 3000,* which is the force actually available for re-starting the discharge if momentarily stopped.

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* A still higher voltage on open circuit would be preferable.

With this discharge, the rate of absorption of mixed gases is about 7 litres per hour. When the argon has accumulated to a considerable extent, the rate falls off, and after several days' work, about 6 litres per hour becomes the maximum. In commencing operations it is advisable to introduce, first, the oxygen necessary to combine with the already included air, after which the feed of mixed gases should consist of about 11 parts of oxygen to 9 parts of air. The mixed gases may be contained in a large gas-holder, and then, the feed being automatic, very little attention is required. When it is desired to determine the rate of absorption, auxiliary gas-holders of glass, graduated into litres, are called into play. If the rate is unsatisfactory, a determination may be made of the proportion of oxygen in the working vessel, and the necessary gas, air, or oxygen, as the case may be, introduced directly.

In re-starting the arc after a period of intermission, it is desirable to cut off the connection with the principal gas-holder. The gas (about two litres in amount) ejected from the working vessel by the expansion is then retained in the auxiliary holder, and no argon finds its way further back. The connection between the working vessel and the auxiliary holder should be made without india-rubber, which is liable to be attacked by the ozonized gases.

The apparatus has been kept in operation for fourteen hours continuously, and there should be no difficulty in working day and night. An electric signal could easily be arranged to give notice of the extinction of the arc, which sometimes occurs unexpectedly; or an automatic device for re-striking the arc could be contrived.—*April*, 1895.]

9. *Density of Argon prepared by means of Oxygen.*

A first estimate of the density of argon prepared by the oxygen method was founded upon the data recorded already respecting the volume present in air, on the assumption that the accurately known densities of "atmospheric" and of chemical nitrogen differ on account of the presence of argon in the former, and that during the treatment with oxygen nothing is oxidised except nitrogen. Thus, if

D = density of chemical nitrogen,
D' = " atmospheric nitrogen,
d = " argon,
α = proportional volume of argon in atmospheric nitrogen,

the law of mixtures gives

$$\alpha d + (1 - \alpha) D = D$$

or

$$d = D + (D' - D)/\alpha.$$

In this formula $D' - D$ and α are both small, but they are known with fair accuracy. From the data already given for the experiment of September 8th

$$\alpha = \frac{65}{0{\cdot}79 \times 7925} = 0{\cdot}0104\,;$$

whence, if on an arbitrary scale of reckoning $D = 2{\cdot}2990$, $D' = 2{\cdot}3102$, we find $d = 3{\cdot}378$. Thus if N_2 be 14, or O_2 be 16, the density of argon is 20·6.

Again, from the January experiment,

$$\alpha = \frac{75{\cdot}0}{7308} = 0{\cdot}0103\,;$$

whence, if $N = 14$, the density of argon is 20·6, as before. There can be little doubt, however, that these numbers are too high, the true value of α being greater than is supposed in the above calculations.

A direct determination by weighing is desirable, but hitherto it has not been feasible to collect by this means sufficient to fill the large globe (§ 1) employed for other gases. A *mixture* of about 400 cub. centims. of argon with pure oxygen, however, gave the weight 2·7315, 0·1045 in excess of the weight of oxygen, viz., 2·6270. Thus, if α be the ratio of the volume of argon to the whole volume, the number for argon will be

$$2{\cdot}6270 + 0{\cdot}1045/\alpha.$$

The value of α, being involved only in the excess of weight above that of oxygen, does not require to be known very accurately. Sufficiently concordant analyses by two methods gave $\alpha = 0{\cdot}1845$; whence, for the weight of the gas we get 3·193; so that if $O = 16$, the density of the gas would be 19·45. An allowance for residual nitrogen, still visible in the gas before admixture of oxygen, raises this number to 19·7, which may be taken as the density of pure argon resulting from this determination.*

10. *Density of Argon Prepared by means of Magnesium.*†

It has already been stated that the density of the residual gas from the first and preliminary attempt to separate oxygen and nitrogen from air by means of magnesium was 19·086, and allowing for contraction on sparking with oxygen the density is calculable as 20·01. The following determinations of density were also made:—

(*a*.) After absorption in glass tubes, the water circulator having been used, and subsequent circulation by means of mercury circulator until rate of contraction had

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* [The proportion of nitrogen (4 or 5 per cent. of the volume) was estimated from the appearance of the nitrogen lines in the spectrum, these being somewhat more easily visible than when 3 per cent. of nitrogen was introduced into pure argon (§ 8).—April, 1895.]

† See Addendum, p. 237.

become slow, 162·843 cub. centims., measured at 757·7 millims. (corr.) pressure, and 16·81° C., weighed 0·2683 grm. Hence,

Weight of 1 litre at 0° and 760 millims. . . .	1·7543 grms.
Density compared with hydrogen (O = 16) . .	19·63 ,,

This gas was again circulated over red-hot magnesium for two days. Before circulation it contained nitrogen as was evident from its spectrum ; after circulating, nitrogen appeared to be absent, and absorption had completely stopped. The density was again determined.

(*b*.) 162,843 cub. centims., measured at 745·4 millims. (corr.) pressure, and 17·25° C., weighed 0·2735 grm. Hence,

Weight of 1 litre at 0° and 760 millims. . . .	1·8206 grms.
Density compared with hydrogen (O = 16) . .	20·38 ,,

Several portions of this gas, having been withdrawn for various purposes, were somewhat contaminated with air, owing to leakage, passage through the pump, &c. All these portions were united in the gas-holder with the main stock, and circulated for eight hours, during the last three of which no contraction occurred. The gas removed from the system of tubes by the mercury-pump was not restored to the gas-holder, but kept separate.

(*c*.) 162·843 cub. centims., measured at 758·1 millims. (corr.) pressure, and 17·09° C., weighed 0·27705 grm. Hence,

Weight of 1 litre at 0° and 760 millims. . . .	1·8124 grms.
Density compared with hydrogen (O = 16) . .	20·28 ,,

The contents of the gas-holder were subsequently increased by a mixture of nitrogen and argon from 37 litres of atmospheric nitrogen, and after circulating, density was determined. The absorption was however not complete.

(*d*.) 162·843 cub. centims., measured at 767·6 millims. (corr.) pressure, and 16·31° C., weighed 0·2703 grm. Hence,

Weight of 1 litre at 0° and 760 millims.	1·742 grms.
Density compared with hydrogen (O = 16) . . .	19·49 ,,

The gas was further circulated, until all absorption had ceased. This took about six hours. Density was again determined.

(*e*.) 162·843 cub. centims. measured at 767·7 millims. (corr.) pressure, and 15·00° C., weighed 0·2773 grm. Hence,

Weight of 1 litre at 0° and 760 millims. . . .	1·7784 grms.
Density compared with hydrogen (O = 16) . .	19·90 ,,

(*f.*) A second determination was carried out, without further circulation.

162·843 cub. centims. measured at 769·0 millims. (corr.) pressure, and 16·00° C., weighed 0·2757 grm. Hence,

Weight of 1 litre at 0° and 760 millims.	1·7713 grms.
Density compared with hydrogen (O = 16)	19·82 ,,

(*g.*) After various experiments had been made with the same sample of gas, it was again circulated until all absorption ceased. A vacuum-tube was filled with it, and showed no trace of nitrogen.

The density was again determined :—

162·843 cub. centims. measured at 750 millims. (corr.) pressure, and at 15·62° C., weighed 0·26915 grm.

Weight of 1 litre at 0° and 760 millims.	1·7707 grms.
Density compared with hydrogen (O = 16). . . .	19·82 ,,

These comprise all the determinations of density made. It should be stated that there was some uncertainty discovered later about the weight of the vacuous globe in (*b*) and (*c*). Rejecting these weighings, the mean of (*e*), (*f*), and (*g*) is 19·88. The density may be taken as 19·9, with approximate accuracy.

It is better to leave these results without comment at this point, and to return to them later.

11. *Spectrum of Argon.*

Vacuum tubes were filled with argon prepared by means of magnesium at various stages in this work, and an examination of these tubes has been undertaken by Mr. Crookes, to whom we wish to express our cordial thanks for his kindness in affording us helpful information with regard to its spectrum. The first tube was filled with the early preparation of density 19·09, which obviously contained some nitrogen. A photograph of the spectrum was taken, and compared with a photograph of the spectrum of nitrogen, and it was at once evident that a spectrum different from that of nitrogen had been registered.

Since that time many other samples have been examined.

The spectrum of argon, seen in a vacuum tube of about 3 millims. pressure, consists of a great number of lines, distributed over almost the whole visible field. Two lines are specially characteristic; they are less refrangible than the red lines of hydrogen or lithium, and serve well to identify the gas when examined in this way. Mr. Crookes, who gives a full account of the spectrum in a separate communication, has kindly furnished us with the accurate wave-lengths of these lines as well as of some others next to be described; they are respectively 696·56 and 705·64 $\times 10^{-6}$ millim.

Besides these red lines, a bright yellow line, more refrangible than the sodium line, occurs at 603·84. A group of five bright green lines occurs next, besides a number of less intensity. Of this group of five, the second, which is perhaps the most brilliant, has the wave-length 561·00. There is next a blue, or blue-violet, line of wave-length 470·2 and last, in the less easily visible part of the spectrum, there are five strong violet lines, of which the fourth, which is the most brilliant, has the wave-length 420·0.

Unfortunately, the red lines, which are not to be mistaken for those of any other substance, are only to be seen at atmospheric pressure when a very powerful jar-discharge is passed through argon. The spectrum, seen under these conditions, has been examined by Professor SCHUSTER. The most characteristic lines are perhaps those in the neighbourhood of F, and are very easily seen if there be not too much nitrogen, in spite of the presence of some oxygen and water-vapour. The approximate wave-lengths are :—

487·91	Strong.
(486·07)	F.
484·71	Not quite so strong.
480·52	Strong.
476·50 473·53 472·56 }	Fairly strong characteristic triplet.

It is necessary to anticipate Mr. CROOKES's communication, and to state that when the current is passed from the induction-coil in one direction, that end of the capillary tube next the positive pole appears of a redder, and that next the negative of a bluer hue. There are, in effect, two spectra, which Mr. CROOKES has succeeded in separating to a considerable extent. Mr. E. C. C. BALY,* who has noticed a similar phenomenon, attributes it to the presence of two gases. The conclusion would follow that what we have termed "argon" is in reality a mixture of two gases which have as yet not been separated. This conclusion, if true, is of great importance, and experiments are now in progress to test it by the use of other physical methods. The full bearing of this possibility will appear later.

A comparison was made of the spectrum seen in a vacuum tube with the spectrum in a "plenum" tube, *i.e.*, one filled at atmospheric pressure. Both spectra were thrown into a field at the same time. It was evident that they were identical, although the relative strengths of the lines were not always the same. The seventeen most striking lines were absolutely coincident.

The presence of a small quantity of nitrogen interferes greatly with the argon spectrum. But we have found that in a tube with platinum electrodes, after the

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* 'Proc. Phys. Soc.,' 1893, p. 147. He says: "When an electric current is passed through a mixture of two gases, one is separated from the other, and appears in the negative glow."

discharge has been passed for four hours, the spectrum of nitrogen disappears, and the argon spectrum manifests itself in full purity. A specially constructed tube, with magnesium electrodes, which we hoped would yield good results, removed all traces of nitrogen it is true, but hydrogen was evolved from the magnesium, and showed its characteristic lines very strongly. However, these are easily identified. The gas evolved on heating magnesium *in vacuo*, as proved by a separate experiment, consists entirely of hydrogen.

Mr. Crookes has proved the identity of the chief lines of the spectrum of gas separated from air-nitrogen by aid of magnesium with that remaining after sparking air-nitrogen with oxygen, in presence of caustic soda solution.

Professor Schuster has also found the principal lines identical in the spectra of the two gases, when taken from the jar discharge at atmospheric pressure.

12. *Solubility of Argon in Water.*

The tendency of the gas to disappear when manipulated over water in small quantities having suggested that it might be more than usually soluble in that liquid, special experiments were tried to determine the degree of solubility.

The most satisfactory measures relating to the gas isolated by means of oxygen were those of September 28. The sample contained a trace of oxygen, and (as judged by the spectrum) a residue of about 2 per cent. of nitrogen. The procedure and the calculations followed pretty closely the course marked out by Bunsen,* and it is scarcely necessary to record the details. The quantity of gas operated upon was about 4 cub. centims., of which about 1½ cub. centims. were absorbed. The final result for the solubility was 3·94 per 100 of water at 12° C., about 2½ times that of nitrogen. Similar results have been obtained with argon prepared by means of magnesium. At a temperature of 13·9°, 131 arbitrary measures of water absorbed 5·3 of argon. This corresponds to a solubility in distilled water, previously freed from dissolved gas by boiling *in vacuo* for a quarter of an hour, and admitted to the tube containing argon without contact with air, of 4·05 cub. centims. of argon per 100 of water.

The fact that the gas is more soluble than nitrogen would lead us to expect it in increased proportion in the dissolved gases of rain water. Experiment has confirmed this anticipation. Some difficulty was at first experienced in collecting a sufficiency for the weighings in the large globe of nearly 2 litres capacity. Attempts at extraction by means of a Töpler pump without heat were not very successful. It was necessary to operate upon large quantities of water, and then the pressure of the liquid itself acted as an obstacle to the liberation of gas from all except the upper layers. Tapping the vessel with a stick of wood promotes the liberation of gas in a

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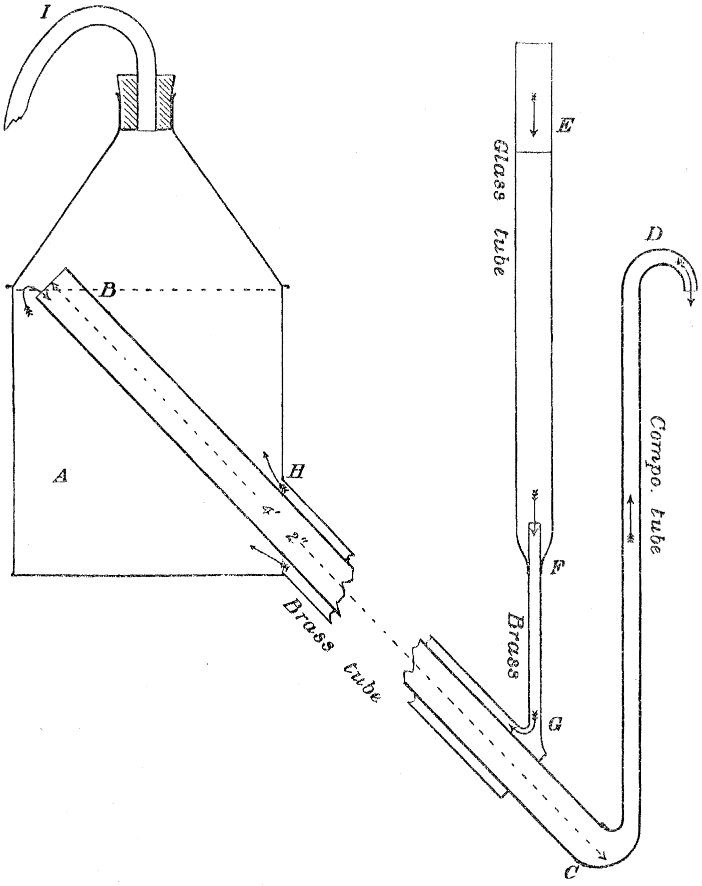
* 'Gasometry,' p. 141.

remarkable manner, but to make this method effective, some means of circulating the water would have to be introduced.

The extraction of the gases by heat proved to be more manageable. Although a large quantity of water has to be brought to or near 100° C., a prolonged boiling is not necessary, as it is not a question of collecting the whole of the gas contained in the water. The apparatus employed, which worked very well after a little experience, will be understood from the accompanying figure. The boiler A was constructed from an old oil-can, and was heated by an ordinary ring Bunsen burner. For the supply and removal of water, two co-axial tubes of thin brass, and more than four feet in length, were applied upon the regenerative principle. The outgoing water flowed in the inner tube BC, continued from C to D by a prolongation of composition tubing. The inflowing water from a rain-water cistern was delivered into a glass tube at E, and passed through a brass connecting tube FG into the narrow annular space between the two principal tubes GH. The neck of the can was fitted with an india-rubber cork and delivery-tube, by means of which the gases were collected in

Fig. 8.



the ordinary way. Any carbonic anhydride was removed by alkali before passage into the glass aspirating bottles used as gas-holders.

The convenient working of this apparatus depends very much upon the maintenance of a suitable relation between the heat and the supply of water. It is desirable that the water in the can should actually boil, but without a great development of steam; otherwise not only is there a waste of heat, and thus a smaller yield of gas, but the inverted flask used for the collection of the gas becomes inconveniently hot and charged with steam. It was found desirable to guard against this by the application of a slow stream of water to the external surface of the flask. When the supply of water is once adjusted, nearly half a litre of gas per hour can be collected with very little attention.

The gas, of which about four litres are required for each operation, was treated with red-hot copper, cupric oxide, sulphuric acid, potash, and finally phosphoric anhydride, exactly as atmospheric nitrogen was treated in former weighings. The weights found, corresponding to those recorded in § 1, were on two occasions, 2·3221 and 2·3227, showing an excess of 24 milligrms. above the weight of true nitrogen. Since the corresponding excess for atmospheric nitrogen is 11 milligrms., we conclude that the water-nitrogen is relatively twice as rich in argon.

Unless some still better process can be found, it may be desirable to collect the gases ejected from boilers, or from large supply pipes which run over an elevation, with a view to the preparation of argon upon a large scale.

The above experiments relate to rain water. As regards spring water, it is known that many thermal springs emit considerable quantities of gas, hitherto regarded as nitrogen. The question early occurred to us as to what proportion, if any, of the new gas was contained therein. A notable example of a nitrogen spring is that at Bath, examined by DAUBENY in 1833. With the permission of the authorities of Bath, Dr. ARTHUR RICHARDSON was kind enough to collect for us about 10 litres of the gases discharged from the King's Spring. A rough analysis on reception showed that it contained scarcely any oxygen and but little carbonic anhydride. Two determinations of density were made, the gas being treated in all respects as air, prepared by diffusion and unprepared, were treated for the isolation of atmospheric nitrogen. The results were :—

October 29	2·30513
November 7	2·30532
Mean	2·30522

The weight of the "nitrogen" from the Bath gas is thus about halfway between that of chemical and "atmospheric" nitrogen, suggesting that the proportion of argon is *less* than in air, instead of greater as had been expected.

13. *Behaviour at Low Temperatures.*

A single experiment was made with an early sample of gas, of density 19·1, which certainly contained a considerable amount of nitrogen. On compressing it in a pressure apparatus to between 80 and 100 atmospheres pressure, and cooling to − 90° by means of boiling nitrous oxide, no appearance of liquefaction could be observed. As the critical pressure was not likely to be so high as the pressure to which it had been exposed, the non-liquefaction was ascribed to insufficient cooling.

This supposition turned out to be correct. For, on sending a sample to Professor Olszewski, the author of most of the accurate measurements of the constants of gases at low temperatures, he was kind enough to submit it to examination. His results are published elsewhere; but, for convenience of reference, his tables, showing vapour-pressures, and giving a comparison between the constants of argon and those of other gases, are here reproduced.

VAPOUR-PRESSURES.

Temperature.	Pressure.	Temperature.	Pressure.	Temperature.	Pressure.
− 186°·9	740·5 millims.	− 136°·2	27·3 atms.	− 129°·4	35·8 atms.
− 139·1	23·7 atms.	− 135·1	29·0 ,,	− 128·6	38·0 ,,
− 138·3	25·3 ,,	− 134·4	29·8 ,,	− 121·0	50·6 ,,

Gas.	Critical temperature.	Critical pressure.	Boiling-point.	Freezing-point.	Freezing pressure.	Density of gas.	Density of liquid at boiling-point.	Colour of liquid.
		atms.	°	°	millims.			
Hydrogen, H_2 . . .	Below −220·0°	20·0	?	?	?	1	?	Colourless
Nitrogen, N_2	−146·0	35·0	−194·4	−214·0	60	14	0·885	,,
Carbon monoxide, CO	−139·5	35·5	−190·0	−207·0	100	14	?	,,
Argon, A_1	−121·0	50·6	−186·9	−189·6	?	19·9	About 1·5	,,
Oxygen, O_2	−118·8	50·8	−182·7	?	?	16	1·124	Bluish
Nitric oxide, NO . .	− 93·5	71·2	−153·6	−167·0	138	15	?	Colourless
Methane, CH_4 . . .	− 81·8	54·9	−164·0	−185·8	80	8	0·415	,,

14. *The ratio of the Specific Heats of Argon.**

In order to decide regarding the elementary or compound nature of argon, experiments were made on the velocity of sound in it. It will be remembered that from the velocity of sound, the ratio of the specific heat at constant pressure to that at constant volume can be deduced by means of the equation

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* See Addendum, p. 239.

$$n\lambda = v = \sqrt{\left\{\frac{e}{d}(1 + \alpha t)\frac{C_p}{C_v}\right\}},$$

where n is the frequency, λ is the wave-length of sound, v its velocity, e the isothermal elasticity, d the density, $(1 + \alpha t)$ the temperature-correction, C_p the specific heat at constant pressure, and C_v that at constant volume. In comparing two gases at the same temperature, each of which obeys BOYLE's law with sufficient approximation and in using the same sound, many of these factors disappear, and the ratio of specific heats of one gas may be deduced from that of the other, if known, by the simple proportion

$$\lambda^2 d : \lambda'^2 d' : : 1{\cdot}408 : x,$$

where for example λ and d refer to air, of which the ratio is 1·408, according to the mean of observations by RÖNTGEN (1·4053), WÜLLNER (1·4053), KAYSER (1·4106), and JAMIN and RICHARD (1·41).

The apparatus employed, although in principle the same as that usually employed, differed somewhat from the ordinary pattern, inasmuch as the tube was a narrow one, of 2 millims. bore, and the vibrator consisted of a glass rod, sealed into one end of the tube, so that about 15 centims. projected outside the tube, while 15 centims. was contained in the tube. By rubbing the projecting part longitudinally with a rag wet with alcohol, vibrations of exceedingly high pitch of the gas contained in the tube took place, causing waves which registered their nodes by the usual device of lycopodium powder. The temperature was that of the atmosphere and varied little from 17·5°; the pressure was also atmospheric, and varied only one millim. during the experiments. Much of the success of these experiments depends on so adjusting the length of the tube as to secure a good echo, else the wave-heaps are indistinct. But this is easily secured by attaching to its open end a piece of thick-walled india-rubber tubing, which can be closed by a clip at a spot which is found experimentally to produce good heaps at the nodes.

The accuracy of this instrument has frequently been tested; but fresh experiments were made with air, carbon dioxide, and hydrogen, so as to make certain that reasonably reliable results were obtainable. Of these an account is here given.

Gas in tube.	Number of observations.		Half-wave-length.		Ratio $\frac{C_p}{C_v}$.	
	I.	II.	I.	II.		
Air	3	2	19·60	19·59	1·408	Assumed
CO_2	3	..	15·11	..	1·276	Found
H_2	3	..	73·6	..	1·376	Found

To compare these results with those of previous observers, the following numbers were obtained for carbon dioxide:—CAZIN, 1·291; RÖNTGEN, 1·305; DE LUCCHI, 1·292; MÜLLER, 1·265; WÜLLNER, 1·311; DULONG, 1·339; MASSON, 1·274; REGNAULT, 1·268; AMAGAT, 1·299; and JAMIN and RICHARD, 1·29. It appears just to reject DULONG's number, which deviates so markedly from the rest; the mean of those remaining is 1·288, which is in sufficient agreement with that given above. For the ratio of the specific heats of hydrogen, we have:—CAZIN, 1·410; RÖNTGEN, 1·385; DULONG, 1·407; MASSON, 1·401; REGNAULT, 1·400; and JAMIN and RICHARD, 1·410. The mean of these numbers is 1·402. This number appears to differ considerably from the one given above. But it must be noted, first, that the wave-length which should have been found is 74·5, a number differing but little from that actually found; second, that the waves were long and that the nodes were somewhat difficult to place exactly; and third, that the atomic weight of hydrogen has been taken as unity, whereas it is more likely to be 1·01, if oxygen, as was done, be taken as 16. The atomic weight 1·01 raises the found value of the ratio to 1·399, a number differing but little from the mean value found by other observers.

Having thus established the trustworthiness of the method, we proceed to describe our experiments with argon.

Five series of measurements were made with the sample of gas of density 19·82. It will be remembered that a previous determination with the same gas gave as its density 19·90. The mean of these two numbers was therefore taken as correct, viz., 19·86.

The individual measurements are:—

I.	II.	III.	IV.	V.	Mean.
18·16	18·14	18·02	18·04	18·03	millims. 18·08

for the half-wave-length. Calculating the ratio of the specific heats, the number 1·644 is obtained.

The narrowness of the tube employed in these experiments might perhaps raise a doubt regarding the accuracy of the measurements, for it is conceivable that in so narrow a tube the viscosity of the gas might affect the results. We therefore repeated the experiments, using a tube of 8 millims. internal diameter.

The mean of eleven readings with air, at 18°, gave a half-wave-length of 34·62 millims. With argon in the same tube, and at the same temperature, the half-wave-length was, as a mean of six concordant readings, 31·64 millims. The density of this sample of argon, which had been transferred from a water gas-holder to a mercury gas-holder, was 19·82; and there is some reason to suspect the presence of a trace of air, for it had been standing for some time.

The result, however, substantially proves that the ratio previously found was correct. In the wide tube, $C_p : C_v :: 1{\cdot}61 : 1$. Hence the conclusion must be accepted that the ratio of specific heats is practically $1{\cdot}66 : 1$.

It will be noticed that this is the theoretical ratio for a monatomic gas, that is, a gas in which all energy imparted to it at constant volume is expended in effecting translational motion. The only other gas of which the ratio of specific heats has been found to fulfil this condition is mercury at a high temperature.* The extreme importance of these observations will be discussed later.

15. *Attempts to induce Chemical Combination.*

A great number of attempts were made to induce chemical combination with the argon obtained by use of magnesium, but without any positive result. In such a case as this, however, it is necessary to chronicle negative results, if for no other reason but that of justifying its name, "argon." These will be detailed in order.

(*a*) *Oxygen in Presence of Caustic Alkali.*—This need not be further discussed here; the method of preparing argon is based on its inactivity under such conditions.

(*b*) *Hydrogen.*—It has been mentioned that, in order to free argon from excess of oxygen, hydrogen was admitted, and sparks passed to cause combination of hydrogen and oxygen. Here again caustic alkali was present, and argon appeared to be unaffected.

A separate experiment was, however, made in absence of water, though no special pains was taken to dry the mixture of gases. The argon was admitted up to half an atmosphere pressure into a bulb, through whose sides passed platinum wires, carrying pointed poles of gas-carbon. Hydrogen was then admitted until atmospheric pressure had been attained. Sparks were then passed for four hours by means of a large induction coil, actuated by four storage cells. The gas was confined in a bulb closed by two stop-cocks, and a small V-tube with bulbs was interposed, to act as a gauge, so that if expansion or contraction had taken place, the escape or entry of gas would be observable. The apparatus, after the passage of sparks, was allowed to cool to the temperature of the atmosphere, and, on opening the stop-cock, the level of water in the V-tube remained unaltered. It may therefore be concluded that, in all probability, no combination has occurred; or, that if it has, it was attended with no change of volume.

(*c*) *Chlorine.*—Exactly similar experiments were performed with dry, and afterwards with moist, chlorine. The chlorine had been stored over strong sulphuric acid for the first experiment, and came in contact with dry argon. Three hours sparking produced no change of volume. A drop of water was admitted into the bulb. After four hours sparking, the volume of the gas, after cooling, was diminished by about

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* Kundt and Warburg, 'Pogg. Ann.,' 157, p. 353, 1876.

$\frac{1}{10}$ cub. centim., due probably to the solution of a little chlorine in the small quantity of water present.

(*d*) *Phosphorus.*—A piece of combustion-tubing, closed at one end, containing at the closed end a small piece of phosphorus, was sealed to the mercury reservoir containing argon; connected to the same reservoir was a mercury gauge and a SPRENGEL's pump. After removing all air from the tubes, argon was admitted to a pressure of 600 millims. The middle portion of the combustion-tube was then heated to bright redness, and the phosphorus was distilled slowly from back to front, so that its vapour should come into contact with argon at a red heat. When the gas was hot, the level of the gauge altered; but, on cooling, it returned to its original level, showing that no contraction had taken place. The experiment was repeated several times, the phosphorus being distilled through the red-hot tube from open to closed end, and *vice versâ*. In each case, on cooling, no change of pressure was remarked. Hence it may be concluded that phosphorus at a red-heat is without action on argon. It may be remarked parenthetically that no gaseous compound of phosphorus is known, which does not possess a volume different from the sum of those of its constituents. That no solid compound was formed is sufficiently proved by the absence of contraction. The phosphorus was largely converted into the red modification during the experiment.

(*e*) *Sulphur.*—An exactly similar experiment was performed with sulphur, again with negative results. It may therefore be concluded that sulphur and argon are without action on each other at a red heat. And again, no gaseous compound of sulphur is known in which the volume of the compound is equal to the sum of those of its constituents.

(*f*) *Tellurium.*—As this element has a great tendency to unite with heavy metals, it was thought worth while to try its action. In this, and in the experiments to be described, a different form was given to the apparatus. The gas was circulated over the reagent employed, a tube containing it being placed in the circuit. The gas was dried by passage over soda-lime and phosphoric anhydride; it then passed over the tellurium or other reagent, then through drying tubes, and then back to the gas-holder. That combination did not occur was shown by the unchanged volume of gas in the gas-holder; and it was possible, by means of the graduated cylinder which admitted water to the gas-holder, to judge of as small an absorption as half a cubic centimeter. The tellurium distilled readily in the gas, giving the usual yellow vapours; and it condensed, quite unchanged, as a black sublimate. The volume of the gas, when all was cold, was unaltered.

(*g*) *Sodium.*—A piece of sodium, weighing about half a gramme, was heated in argon. It attacked the glass of the combustion tube, which it blackened, owing to liberation of silicon; but it distilled over in drops into the cold part of the tube. Again no change of volume occurred, nor was the surface of the distilled sodium tarnished; it was brilliant, as it is when sodium is distilled *in vacuo*. It may probably also be concluded from this experiment that silicon, even while being liberated, is without action on argon.

The action of compounds was then tried; those chosen were such as lead to oxides or sulphides. Inasmuch as the platinum-metals, which are among the most inert of elements, are attacked by fused caustic soda, its action was investigated.

(*h*) *Fused and Red-hot Caustic Soda.*—The soda was prepared from sodium, in an iron boat, by adding drops of water cautiously to a lump of the metal. When action had ceased, the soda was melted, and the boat introduced into a piece of combustion-tube placed in the circuit. After three hours circulation no contraction had occurred. Hence caustic soda has no action on argon.

(*i*) *Soda-lime at a red-heat.*—Thinking that the want of porosity of fused caustic soda might have hindered absorption, a precisely similar experiment was carried out with soda-lime, a mixture which can be heated to bright redness without fusion. Again no result took place after three hours heating.

(*j*) *Fused Potassium Nitrate* was tried under the impression that oxygen plus a base might act where oxygen alone failed. The nitrate was fused, and kept at a bright red heat for two hours, but again without any diminution in volume of the argon.

(*k*) *Sodium Peroxide.*—Yet another attempt was made to induce combination with oxygen and a base, by heating sodium peroxide to redness in a current of argon for over an hour, but also without effect. It is to be noticed that metals of the platinum group would have entered into combination under such treatment.

(*l*) *Persulphides of Sodium and Calcium.*—Soda-lime was heated to redness in an open crucible, and some sulphur was added to the red-hot mass, the lid of the crucible being then put on. Combination ensued, with formation of polysulphides of sodium and calcium. This product was heated to redness for three hours in a brisk current of argon, again with negative result. Again, metals of the platinum group would have combined under such treatment.

(*m*) Some argon was shaken in a tube with nitro-hydrochloric acid. On addition of potash, so as to neutralise the acid, and to absorb the free chlorine and nitrosyl chloride, the volume of the gas was barely altered. The slight alteration was evidently due to solubility in the aqueous liquid, and it may be concluded that no chemical action took place.

(*n*) Bromine-water was also without effect. The bromine vapour was removed with potash.

(*o*) A mixture of potassium permanganate and hydrochloric acid, involving the presence of nascent chlorine, had no action, for on absorbing chlorine by means of potash, no alteration in volume had occurred.

(*p*) Argon is not absorbed by platinum black. A current was passed over a pure specimen of this substance; as usual, however, it contained occluded oxygen. There was no absorption in the cold. At 100°, no action took place; and on heating to redness, by which the black was changed to sponge, still no evidence of absorption was noticed. In all these experiments, absorption of half a cubic centimetre of argon could have at once been detected.

We do not claim to have exhausted the possible reagents. But this much is certain, that the gas deserves the name "argon," for it is a most astonishingly indifferent body, inasmuch as it is unattacked by elements of very opposite character, ranging from sodium and magnesium on the one hand, to oxygen, chlorine, and sulphur on the other. It will be interesting to see if fluorine also is without action, but for the present that experiment must be postponed, on account of difficulties of manipulation.

It will also be necessary to try whether the inability of argon to combine at ordinary or at high temperatures is due to the instability of its possible compounds, except when cold. Mercury vapour at 800° would present a similar instance of passive behaviour.

16. *General Conclusions.*

It remains, finally, to discuss the probable nature of the gas or gases which we have succeeded in separating from atmospheric air, and which has been provisionally named *argon*.

That argon is present in the atmosphere, and is not manufactured during the process of separation is amply proved by many lines of evidence. First, atmospheric nitrogen has a high density, while chemical nitrogen is lighter. That chemical nitrogen is a uniform substance is proved by the identity of properties of samples prepared by several different processes, and from several different compounds. It follows, therefore, that the cause of the high density of atmospheric nitrogen is due to the admixture with heavier gas. If that gas possesses the density of 20 compared with hydrogen as unity, atmospheric nitrogen should contain of it approximately 1 per cent. This is found to be the case, for on causing the nitrogen of the atmosphere to combine with oxygen in presence of alkali, the residue amounted to about 1 per cent.; and on removing nitrogen with magnesium the result is similar.

Second: This gas has been concentrated in the atmosphere by diffusion. It is true that it cannot be freed from oxygen and nitrogen by diffusion, but the process of diffusion increases relatively to nitrogen the amount of argon in that portion which does not pass through the porous walls. That this is the case is proved by the increase of density of that mixture of argon and nitrogen.

Third: On removing nitrogen from "atmospheric nitrogen" by means of magnesium, the density of the residue increases proportionately to the concentration of the heavier constituent.

Fourth: As the solubility of argon in water is relatively high, it is to be expected that the density of the mixture of argon and nitrogen, pumped out of water along with oxygen should, after removal of the oxygen, exceed that of "atmospheric nitrogen." Experiment has shown that the density is considerably increased.

Fifth: It is in the highest degree improbable that two processes, so different from each other, should each manufacture the same product. The explanation is simple if it be granted that these processes merely eliminate nitrogen from "atmospheric nitrogen."

Sixth: If the newly discovered gas were not in the atmosphere, the discrepancies in the density of "chemical" and "atmospheric" nitrogen would remain unexplained.

Seventh: It has been shown that pure nitrogen, prepared from its compounds, leaves a negligible residue when caused to enter into combination with oxygen or with magnesium.

There are other lines of argument which suggest themselves; but we think that it will be acknowledged that those given above are sufficient to establish the existence of argon in the atmosphere.

It is practically certain that the argon prepared by means of electric sparking with oxygen is identical with argon prepared by means of magnesium. The samples have in common:—

First: Spectra which have been found by Mr. CROOKES, Professor SCHUSTER, and ourselves to be practically identical.

Second: They have approximately the same density. The density of argon, prepared by means of magnesium, was 19·9; that of argon, from sparking with oxygen, about 19·7; these numbers are practically identical.

Third: Their solubility in water is the same.

That argon is an element, or a mixture of elements, may be inferred from the observations of § 14. For CLAUSIUS has shown that if K be the energy of translatory motion of the molecules of a gas, and H their whole kinetic energy, then

$$\frac{K}{H} = \frac{3(C_p - C_v)}{2C_v},$$

C_p and C_v denoting as usual the specific heat at constant pressure and at constant volume respectively. Hence, if, as for mercury vapour and for argon (§ 14), the ratio of specific heats $C_p : C_v$ be $1\frac{2}{3}$, it follows that $K = H$, or that the whole kinetic energy of the gas is accounted for by the translatory motion of its molecules. In the case of mercury the absence of interatomic energy is regarded as proof of the monatomic character of the vapour, and the conclusion holds equally good for argon.

The only alternative is to suppose that if argon molecules are di- or polyatomic, the atoms acquire no relative motion, even of rotation, a conclusion improbable in itself and one postulating the sphericity of such complex groups of atoms.

Now a monatomic gas can be only an element, or a mixture of elements; and hence it follows that argon is not of a compound nature.

According to AVOGADRO, equal volumes of gases at the same temperature and pressure, contain equal numbers of molecules. The molecule of hydrogen gas, the density of which is taken as unity, is supposed to consist of two atoms. Its molecular weight is therefore 2. Argon is approximately 20 times as heavy as hydrogen, that is, its molecular weight is 20 times as great as that of hydrogen, or 40. But its molecule is monatomic, hence its atomic weight, or, if it be a mixture, the mean of the atomic weights of the elements in that mixture, taken for the proportion in which they are present, must be 40.

This conclusion rests on the assumption that all the molecules of argon are monatomic. The result of the first experiment is, however, so nearly that required by theory, that there is room for only a small number of molecules of a different character. A study of the expansion of argon by heat is proposed, and would doubtless throw light upon this question.

There is evidence both for and against the hypothesis that argon is a mixture: for, owing to Mr. CROOKES's observations of the dual character of its spectrum; against, because of Professor OLSZEWSKI's statement that it has a definite melting-point, a definite boiling-point, and a definite critical temperature and pressure; and because on compressing the gas in presence of its liquid, pressure remains sensibly constant until all gas has condensed to liquid. The latter experiments are the well-known criteria of a pure substance; the former is not known with certainty to be characteristic of a mixture. The conclusions which follow are, however, so startling, that in our future experimental work we shall endeavour to decide the question by other means.

For the present, however, the balance of evidence seems to point to simplicity. We have, therefore, to discuss the relations to other elements of an element of atomic weight 40. We inclined for long to the view that argon was possibly one, or more than one, of the elements which might be expected to follow fluorine in the periodic classification of the elements—elements which should have an atomic weight between 19, that of fluorine, and 23, that of sodium. But this view is apparently put out of court by the discovery of the monatomic nature of its molecules.

The series of elements possessing atomic weights near 40 are :—

Chlorine	35·5
Potassium	39·1
Calcium	40·0
Scandium	44·0.

There can be no doubt that potassium, calcium, and scandium follow legitimately their predecessors in the vertical columns, lithium, beryllium, and boron, and that they are in almost certain relation with rubidium, strontium, and (but not so certainly) yttrium. If argon be a single element, then there is reason to doubt whether the periodic classification of the elements is complete; whether, in fact, elements may not exist which cannot be fitted among those of which it is composed. On the other hand, if argon be a mixture of two elements, they might find place in the eighth group, one after chlorine and one after bromine. Assuming 37 (the approximate mean between the atomic weights of chlorine and potassium) to be the atomic weight of the lighter element, and 40 the mean atomic weight found, and supposing that the second element has an atomic weight between those of bromine, 80, and rubidium, 85·5, viz., 82, the mixture should consist of 93·3 per cent. of the lighter, and 6·7 per cent. of the heavier element. But it appears improbable that such a high percentage as 6·7 of a heavier element should have escaped detection during liquefaction.

If the atomic weight of the lighter element were 38, instead of 37, however, the proportion of heavier element would be considerably reduced. Still, it is difficult to account for its not having been detected, if present.

If it be supposed that argon belongs to the eighth group, then its properties would fit fairly well with what might be anticipated. For the series, which contains

$$\mathrm{Si}_n^{\mathrm{IV}}, \quad \mathrm{P}_4^{\mathrm{III\ and\ V}}, \quad \mathrm{S}_{8\text{ to }2}^{\mathrm{II\ to\ VI}}, \quad \text{and } \mathrm{Cl}_2^{\mathrm{I\ to\ VII}},$$

might be expected to end with an element of monatomic molecules, of no valency, *i.e.*, incapable of forming a compound, or if forming one, being an octad; and it would form a possible transition to potassium, with its monovalence, on the other hand. Such conceptions are, however, of a speculative nature; yet they may be perhaps excused, if they in any way lead to experiments which tend to throw more light on the anomalies of this curious element.

In conclusion, it need excite no astonishment that argon is so indifferent to reagents. For mercury, although a monatomic element, forms compounds which are by no means stable at a high temperature in the gaseous state; and attempts to produce compounds of argon may be likened to attempts to cause combination between mercury gas at 800° and other elements. As for the physical condition of argon, that of a gas, we possess no knowledge why carbon, with its low atomic weight, should be a solid, while nitrogen is a gas, except in so far as we ascribe molecular complexity to the former and comparative molecular simplicity to the latter. Argon, with its comparatively low density and its molecular simplicity, might well be expected to rank among the gases. And its inertness, which has suggested its name, sufficiently explains why it has not previously been discovered as a constituent of compound bodies.

We would suggest for this element, assuming provisionally that it is not a mixture, the symbol A.

We have to record our thanks to Messrs. GORDON, KELLAS, and MATTHEWS, and especially to Mr. PERCY WILLIAMS, for their assistance in the prosecution of this research.

ADDENDUM (by Professor W. RAMSAY).

March 20, 1895.

Further determinations of the density of argon prepared by means of magnesium have been made. In each case the argon was circulated over magnesium for at least two hours after all absorption of nitrogen had stopped, as well as over red-hot copper, copper oxide, soda-lime, and phosphoric anhydride. The gas also passed out of the mercury gas-holder through phosphoric anhydride into the weighing globe. The results are in complete accordance with previous determinations of density; and for convenience of reference the former numbers are included in the table which follows.

DENSITY of Argon.

Date.	Volume.	Temperature.	Pressure.	Weight.	Weight of 1 litre at 0° and 760 millims.	Density (O = 16).
	cub. centims.	°	millims.	grm.		
(1) Nov. 26 . . .	162·843	15·00	767·7	0·2773	1·7784	19·904
(2) „ 27 . . .	162·843	16·00	769·0	0·2757	1·7717	19·823
(3) Dec. 22 . . .	162·843	15·62	750·1	0·26915	1·7704	19·816
(4) Feb. 16 . . .	162·843	13·45	771·1	0·2818	1·7834	19·959
(5) „ 19 . . .	162·843	14·47	768·2	0·2789	1·7842	19·969
(6) „ 24 . . .	162·843	17·85	764·4	0·2738	1·7810	19·932

The general mean is 19·900; or if Nos. (2) and (3) be rejected as suspiciously low, the mean of the remaining four determinations is 19·941. The molecular weight may therefore be taken as 39·9 without appreciable error.

The value of R in the gas-equation $R = pv/T$ has also been determined between − 89° and + 248°. For this purpose, a gas-thermometer was filled with argon, and a direct comparison was made with a similar thermometer filled with hydrogen.

The method of using such a hydrogen-thermometer has already been described by RAMSAY and SHIELDS.* For the lowest temperature, the thermometer bulbs were immersed in boiling nitrous oxide; for atmospheric temperature, in running water; for temperatures near 100° in steam, and for the remaining temperatures, in the vapours of chlorobenzene, aniline, and quinolene.

The results are collected in the following tables:—

HYDROGEN Thermometer.

Temperature.	Pressure.	Volume (corr.).	R.
° C.	millims.		
13·04	763·6	1·00036	2·6705
99·84	992·6	1·00280	2·6697
130·62	1073·8	1·00364	2·6701
185·46	1218·5	1·00518	2·6716
248·66	1385·1	1·00703	2·6737
− 87·92	497·3	0·99756	2·6804

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* 'Trans. Chem. Soc.,' vol. 63, pp. 835, 836. It is to be noticed that the value of R is not involved in using the hydrogen-thermometer; its constancy alone is postulated.

The value of R is thus practically constant, and this affords a proof that the four last temperatures have been estimated with considerable accuracy.

ARGON Thermometer.

	Temperature.	Pressure.	Volume (corr.).	R.
	° C.	millims.		
Series I. . .	14·15	701·7	1·000396	2·4446
	14·27	699·7	1·000401	2·4366
	14·40	702·6	1·000404	2·4462
	99·96	906·5	1·00280	2·4379
	100·06	904·8	1·00280	2·4322
	−87·92	455·6	0·99756	2·4556
By mischance, air leaked into the bulb; it was therefore refilled.				
Series II. .	130·58	1060·0	1·0037	2·6363
	185·46	1200·3	1·0052	2·6317
A bubble of argon leaked into the bulb, and the value of R increased.				
Series III. .	12·05	760·9	1·00034	2·6698
	12·61	761·3	1·00034	2·6728
	248·66	1384·0	1·0070	2·6717
	248·66	1376·9	1·0070	2·6580
	−87·92	495·7	0·99756	2·6718

It may be concluded from these numbers, that argon undergoes no molecular change between − 88° and + 250°.

Further determinations of the wave-length of sound in argon have been made, the wider tube having been used. In every case the argon was as carefully purified as possible. In experiment (3) too much lycopodium dust was present in the tube; that is perhaps the cause of the low result. For completeness' sake, the original result in the narrow tube has also been given.

Date.	Density.	Half-wave-length.		Temperature.		Ratio.
		In air.	In argon.	Air.	Argon.	
Dec. 6	19·92	19·59	18·08	17°·5	17°·5	1·644
Feb. 15	19·96	33·73	31·00	6·7	6·5	1·641
„ 20	19·97	34·10	31·31	7·22	8·64	1·629
Mar. 19	19·94	34·23	31·68	11·20	11·49	1·659

The general mean of these numbers is 1·643; if (3) be rejected, it is 1·648. In the last experiment every precaution was taken. The half-wave-length in air is the mean of 11 readings, the highest of which was 34·67 and the lowest 34·00. They run :—

34·67 ; 34·06 ; 34·27 ; 34·39 ; 34·00 ; 34·00 ; 34·13 ; 34·20 ; 34·20 ; 34·33 ; 34·33.
11·25° ; 11·00° ; 10·80° ; 10·8° ; 10·0° ; 11·0° ; 11·3° ; 11·4° ; 11·4° ; 11·6° ; 11·6°.

With argon the mean is also that of 11 readings, of which the highest is 31·83, and the lowest, 31·5. They are :—

31·5 ; 31·5 ; 31·66 ; 31·55 ; 31·83 ; 31·77 ; 31·81 ; 31·83 ; 31·83 ; 31·50 ; 31·66.
11·8° ; 11·8° ; 11·20° ; 11·40° ; 11·60° ; 11·40° ; 11·40° ; 11·4° ; 11·5° ; 11·5° ; 11·4°.

If the atomic weight of argon is identical with its molecular weight, it must closely approximate to 39·9. But if there were some molecules of A_2 present, mixed with a much larger number of molecules of A_1, then the atomic weight would be correspondingly reduced. Taking an imaginary case, the question may be put :—What percentage of molecules of A_2 would raise the density of A_1 from 19·0 to 19·9 ? A density of 19·0 would imply an atomic weight of 38·0, and argon would fall into the gap between chlorine and potassium. Calculation shows that in 10,000 molecules, 474 molecules of A_2 would have this result, the remaining 9526 molecules being those of A_1.

Now if molecules of A_2 be present, it is reasonable to suppose that their number would be increased by lowering the temperature, and diminished by heating the gas. A larger change of density should ensue on lowering than on raising the temperature, however, as on the above supposition, there is not a large proportion of molecules of A_2 present.

But it must be acknowledged that the constancy of the found value of R is not favourable to this supposition.

A similar calculation is possible for the ratio of specific heats. Assuming the gas to contain 5 per cent. of molecules of A_2, and 95 per cent. of molecules of A_1 the value of γ, the ratio of specific heats, would be 1·648. All that can be said on this point is, that the found ratio approximates to this number ; but whether the results are to be trusted to indicate a unit in the second decimal appears to me doubtful.

The question must therefore for the present remain open.

ADDENDUM.

April 9.

It appears worth while to chronicle an experiment of which an accident prevented the completion. It may be legitimately asked, Does magnesium not absorb any argon, or any part of what we term argon ? To decide this question, about 500 grms. of magnesium nitride, mixed with metallic magnesium which had remained unacted on, during extraction of nitrogen from "air-nitrogen," was placed in a flask, to which a reservoir full of dilute hydrochloric acid was connected. The flask was coupled with a tube full of red-hot copper oxide, intended to oxidise the hydrogen which would be evolved by the action of the hydrochloric acid on the metallic magnesium. To the end of the copper-oxide tube a gas-holder was attached, so as to collect any evolved gas; and the system was attached to a vacuum-pump, in order to exhaust the apparatus before commencing the experiment, as well as to collect all gas which should be evolved, and remain in the flask.

On admitting hydrochloric acid to the flask of magnesium nitride a violent reaction took place, and fumes of ammonium chloride passed into the tube of copper oxide. These gave, of course, free nitrogen. This had not been foreseen; it would have been well to retain these fumes by plugs of glass-wool. The result of the experiment was that about 200 cub. centims. of gas were collected. After sparking with oxygen in presence of caustic soda, the volume was reduced to 3 cub. centims. of a gas which appeared to be argon