

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	<u>2·31383</u>
Ordinary atmospheric nitrogen	<u>2·31016</u>
Difference	+ ·00367
Globe empty, November 5, 8	2·82355
Globe full, November 6 (eight pipes) . . .	·51011
Weight of gas	<u>2·31344</u>
Ordinary atmospheric nitrogen	<u>2·31016</u>
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.

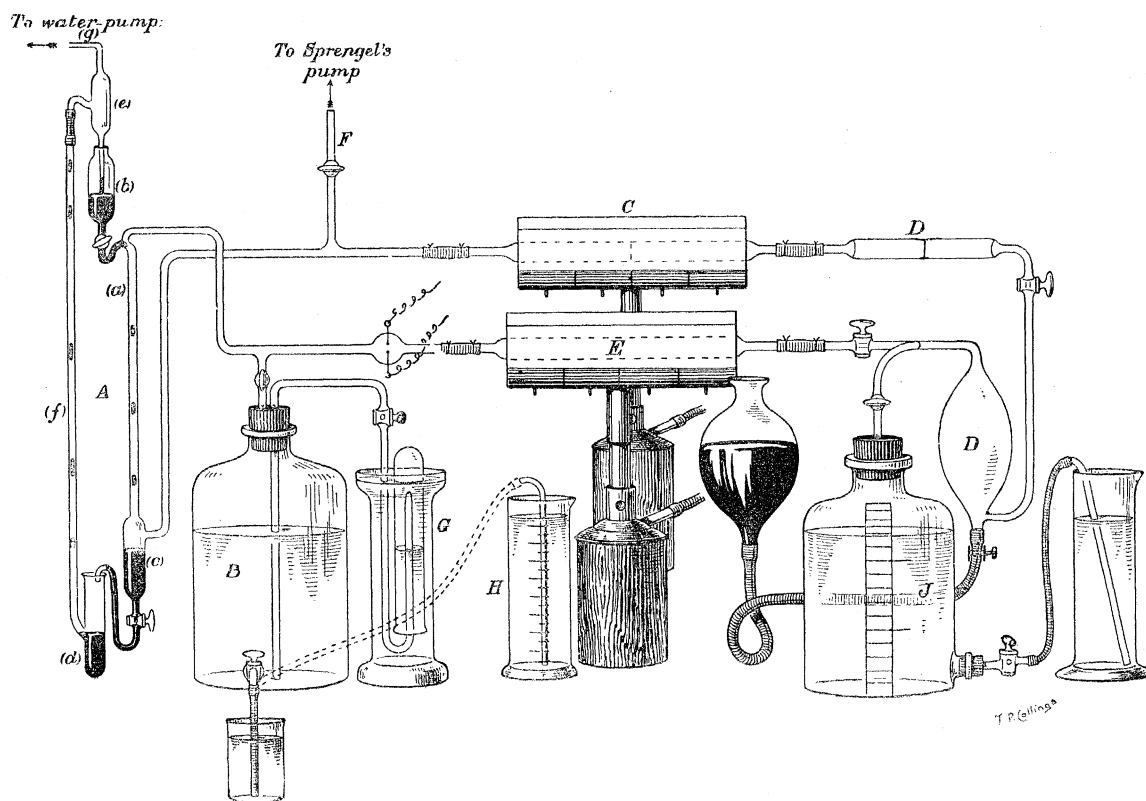
After the iron tube followed a second small U-tube containing water, intended to indicate the rate at which the argon escaped into a small gas-holder placed to receive it. The nitrogen was absorbed rapidly, and argon entered the small gas-holder. But there was reason to suspect that the iron tube is 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.

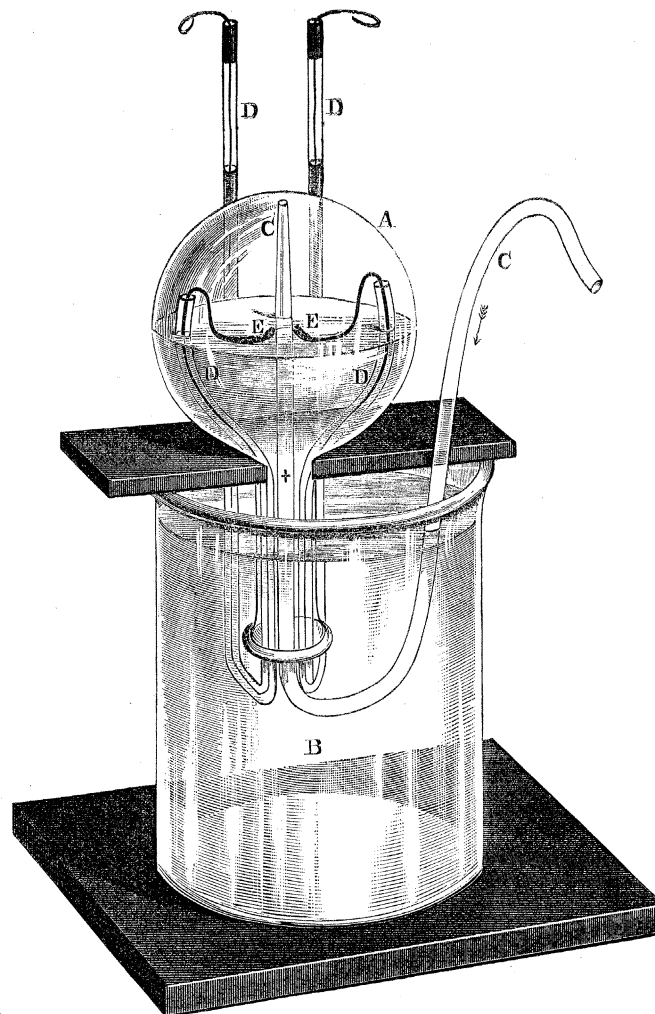
The RUHMKORFF employed in this operation was one of medium size. When the mixture was rightly proportioned and the arc of full length, the rate of absorption was about 700 cub. centims. per hour. A good deal of time is lost in starting, for, especially when there is soda on the platinum, the arc is liable 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

* '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

Fig. 6.



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.

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 $1\frac{1}{2}$ 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.

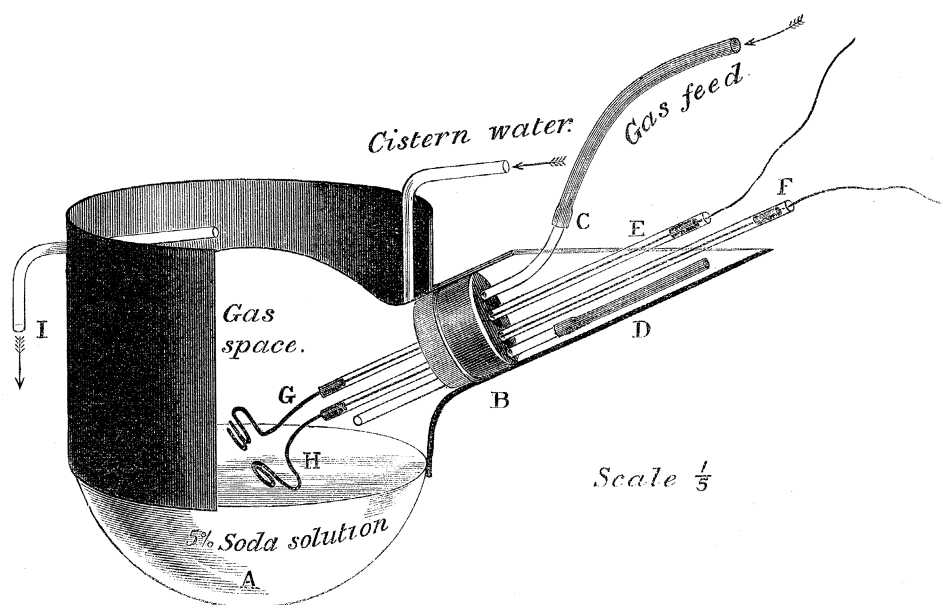
When we attempt to increase the rate of absorption by the use of a more powerful electric arc, further experimental difficulties present themselves. In the arrangement already described, giving an absorption of 700 cub. centims. per hour, the upper part of the flask becomes very hot. With a more powerful 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

Fig. 7.



of stout iron wires terminated by thick platinum, 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.

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 $N + 1.75O$ —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 $2\frac{1}{2}$ 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.

* 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

$$\begin{aligned} D &= \text{density of chemical nitrogen,} \\ D' &= \quad \text{,, atmospheric nitrogen,} \\ d &= \quad \text{,, argon,} \\ \alpha &= \text{proportional volume of argon in atmospheric nitrogen,} \end{aligned}$$

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

$$\alpha = \frac{65}{0.79 \times 7925} = 0.0104;$$

whence, if on an arbitrary scale of reckoning $D = 2.2990$, $D' = 2.3102$, we find $d = 3.378$. Thus if N_2 be 14, or O_2 be 16, the density of argon is 20.6.

Again, from the January experiment,

$$\alpha = \frac{75.0}{7308} = 0.0103;$$

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

$$2.6270 + 0.1045/\alpha.$$

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 $\alpha = 0.1845$; 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

* [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 gm. 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 gm. 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 gm. 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 gm. 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 gm. 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 gm. 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 gm.

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	}	Fairly strong characteristic triplet.
473·53		
472·56		

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

* '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 $1\frac{1}{2}$ cub. centims. were absorbed. The final result for the solubility was 3.94 per 100 of water at 12° C., about $2\frac{1}{2}$ 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.

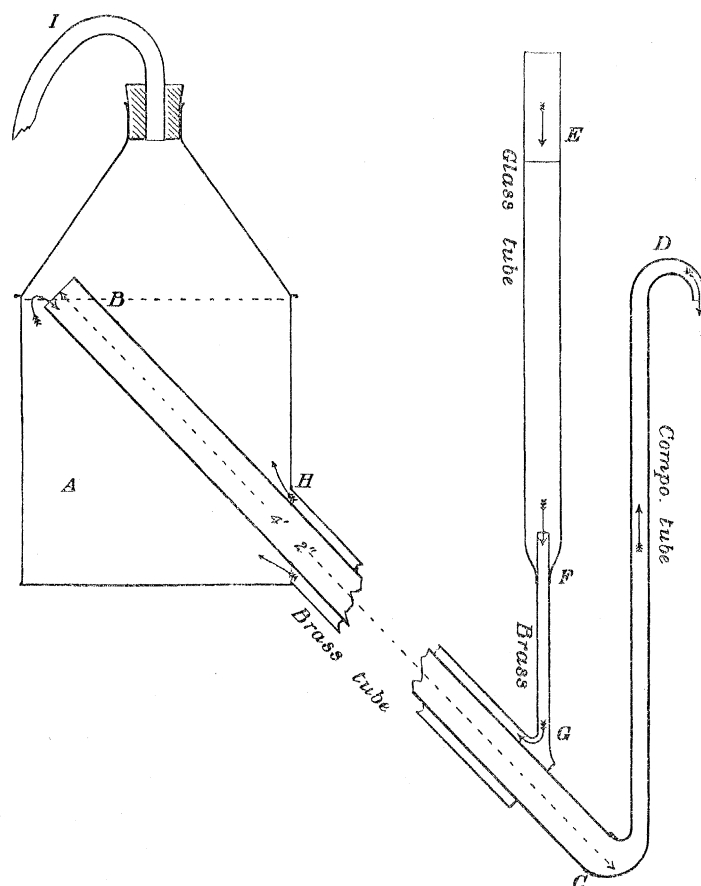
The fact that the gas is more soluble than nitrogen would lead us to expect it in increased proportion in the dissolved gases of rain water. Experiment has confirmed this anticipation. Some difficulty was at first experienced in collecting a sufficiency for the weighings in the large globe of nearly 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

* '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

Fig. 8.



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

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	<u>2·30522</u>

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.