Sidgreaves (Rev. W.)   Notes on Solar Observations at Stonyhurst
    College Observatory.   8vo.   *London* 1894.          The Author.
Walker (G. C.)   Customary Law of the Main Tribes in the Lahore
    District.   Vol. XIII.   8vo.   *Lahore* 1894.          India Office.

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Map showing Lines of Equal Magnetic Declination for January 1,
    1895.   With a Reprint from the ' Colliery Guardian.'
                              The Editor, ' Colliery Guardian.'

*January* 31, 1895.

(In the Theatre of the University of London.)

The LORD KELVIN, D.C.L., LL.D., President, in the Chair.

A List of the Presents received was laid on the table, and thanks
ordered for them.

The following Papers were read :—

I. " Argon, a New Constituent of the Atmosphere."   By
    LORD RAYLEIGH, Sec. R.S., and WILLIAM RAMSAY, F.R.S.,
    Professor of Chemistry, University College, London.
    Received January 31, 1895.

(Abstract.)

I. *Density of Nitrogen from Various Sources.*

In a former paper* it has been shown that nitrogen extracted
from chemical compounds is about $\frac{1}{2}$ per cent. lighter than " atmos-
pheric 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 |

* Rayleigh, " On an Anomaly encountered in Determinations of the Density of
Nitrogen Gas." ' Roy. Soc. Proc.,' vol. 55, p. 340, 1894.

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 hypobromite was prepared from commercial materials in the proportions recommended for the analysis of urea. 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, and 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 mean result, reduced so as to correspond with those above quoted, is 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 ⋃ tube, the surface of the metal was soon fouled.

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 mean result from three fillings is 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 deduction of 0·0006 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 1·2505, that of atmospheric nitrogen being 1·2572.

It is of interest to compare the density of nitrogen obtained from chemical compounds with that of oxygen. We have $N_2 : O_2 = 2·2984 : 2·6276 = 0·87471$; so that if $O_2 = 16$, $N_2 = 13·9954$. 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.

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, Oct. 30, Nov. 5.......... 2·82313
Globe full, Oct. 31 .................. 0·52395
                                      ————
          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

* Rayleigh, "On the Densities of the Principal Gases," 'Roy. Soc. Proc.,' vol. 53, p. 134, 1893.

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 by degrees, 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 mm. pressure, 162·843 c.c. of this nitrogen weighed 0·18963 gram. Hence,

Weight of 1 litre at 0° C. and 760 mm. pressure = 1·2521 gram.

The mean result of the weight of 1 litre of "chemical" nitrogen has been found to equal 1·2505. It is therefore seen that "chemical" nitrogen, derived from "atmospheric" nitrogen, without any exposure to red-hot copper, possesses about 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 standardised by titrating a specimen of pure sublimed ammonium chloride. The silver solution was of such a strength that 1 c.c. precipitated the chlorine from 0·001701 gram of ammonium chloride.

1. Ammonium chloride from orange-coloured sample of magnesium nitride contained 66·35 per cent. of chlorine.

2. Ammonium chloride from blackish magnesium nitride contained 66·35 per cent. of chlorine.

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

## II. *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 high 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, $\frac{1}{2}$ per cent. only by volume would be needed ; or if the density were but half as much again as that of nitrogen, then 1 per cent. would still suffice.    But in

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

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.   This experiment, although in view from the first, was not executed until a later stage of the inquiry (§ VI), when results were 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 ∪ tube.*

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 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

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

† *I.e.*, deprived of oxygen.   " Phlogisticated air " = nitrogen ;  " dephlogisticated air " = oxygen.

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 compounded 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 $\frac{1}{120}$th 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. This was about 1 c.c. per hour, of which two-fifths would be nitrogen.

### III. *Methods of Causing Free Nitrogen to Combine.*

To eliminate nitrogen from air, in order to ascertain whether any other gas could be detected, involves the use of some absorbent. The elements which have been found to combine directly with nitrogen are : boron, silicon, titanium, lithium, strontium, barium, magnesium, aluminium, mercury, and, under the influence of an electric discharge, hydrogen in presence of acid, and oxygen in presence of alkali.

[*] ' Phil. Trans.,' vol. 78, p. 271, 1788.

Besides these, a mixture of barium carbonate and carbon at a high temperature is known to be effective. Of those tried, magnesium in the form of turnings was found to be the best. When nitrogen is passed over magnesium, heated in a tube of hard glass to bright redness, combustion with incandescence begins at the end of the tube through which the gas is introduced, and proceeds regularly until all the metal has been converted into nitride. Between 7 and 8 litres of nitrogen can be absorbed in a single tube; the nitride formed is a porous, dirty orange-coloured substance.

### IV. *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 standing over a large quantity of weak alkali, and the current was conveyed in wires insulated by ∪-shaped glass tubes passing through the liquid round the mouth of the test-tube. With the given battery and coil a somewhat short spark or arc of about 5 mm. 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 c.c. per hour, or thirty 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 c.c. 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 c.c. On treatment with alkaline pyrogallate, the gas shrank to 0·32 c.c. That this small residue could not be nitrogen was argued from the fact that it had withstood the prolonged action of the spark, although mixed with oxygen in nearly the most favourable proportion.

The residue was then transferred to the test-tube with an addition of another 50 c.c. of air, and the whole worked up with oxygen as before. The residue was now 2·2 c.c., and, after removal of oxygen, 0·76 c.c.

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 c.c. of air with 7 c.c. of oxygen was sparked for $1\frac{1}{4}$ hours, the residue was 0·47 c.c., and after removal of oxygen 0·06 c.c. 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. 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.

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

A preliminary experiment carried out by Mr. Percy Williams on the absorption of atmospheric nitrogen, freed from oxygen by means of red-hot copper, in which the gas was not passed over, but simply allowed to remain in contact with the metal, gave a residue of density 14·88. This result, although not conclusive, was encouraging; and an attempt was made, on a larger scale, by passing atmospheric nitrogen backwards and forwards over red-hot magnesium from one large gas-holder to another to obtain a considerable quantity of the heavier gas. In the course of ten days, about 1500 c.c. were collected and transferred gradually to a mercury gas-holder, from which the gas was passed over soda-lime, phosphoric anhydride, magnesium at a red heat, copper oxide, soda-lime, and phosphoric anhydride into a second mercury gas-holder. After some days the gas was reduced in volume to about 200 c.c., and its density was found to be 16·1. After further absorption, in which the volume was still further reduced, the density of the residue was increased to 19·09.

On passing sparks for several hours through a mixture of a small quantity of this gas with oxygen, its volume was still further reduced. Assuming that this reduction was due to the further elimination of nitrogen, the density of the remaining gas was calculated to be 20·0.

The spectrum of the gas of density 19·09, though showing nitrogen bands, showed many other lines which were not recognisable as belonging to any known element.

## VI. *Proof of the Presence of Argon in Air by means of Atmolysis.*

It has already (§ II) 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 ; the other end was connected to a bottle aspirator, initially full of water, and so arranged as to draw about 2 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 2 per cent. was never much exceeded.

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, moisture and carbonic acid by potash and phosphoric anhydride.

In a total weight of approximately 2·3 grams the excess of weight of the diffused nitrogen over ordinary atmospheric nitrogen was in four experiments, 0·0049, 0·0014, 0·0027, 0·0015.

The mean excess of the four determinations is 0·00262 gram, or, if we omit the first, which depended upon a vacuum weighing of two months old, 0·00187 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, in which the excess was I, 0·0037; II, 0·0033.

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 $3\frac{1}{2}$ milligrams on the 11 milligrams, 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.

### VII. *Negative Experiments to prove that Argon is not derived from Nitrogen 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 (§ VI), 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. 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 c.c. This was transferred, and after treatment with alkaline pyrogallate to remove oxygen measured 3·3 c.c. If atmospheric nitrogen had been employed, the final residue should have been about 30 c.c. Of the 3·3 c.c. actually left, a part is accounted for by an accident, 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 c.c. of nitrogen from ammonium nitrite was treated with oxygen. The final residue was 3·5 c.c., and was found to consist mainly of argon.

The source of the residual argon is to be sought in the water used for the manipulation of the large quantities of gas (6 litres of nitrogen and 11 litres of oxygen) employed. When carbonic acid

was collected in a similar manner and subsequently absorbed by potash, it was found to have acquired a contamination consistent with this explanation.

Negative experiments were also carried out, absorbing nitrogen by means of magnesium. In one instance 3 litres of nitrogen prepared from ammonium chloride and bleaching-powder was reduced in volume to 4·5 c.c., and on sparking with oxygen its volume was further reduced to about 3 c.c. The residue appeared to consist of argon. Another experiment, in which 15 litres of nitrogen from ammonium nitrite was absorbed, gave a final residue of 3·5 c.c. Atmospheric nitrogen, in the latter case, would have yielded 150 c.c., hence less than $\frac{1}{40}$th of the normal quantity was obtained. It should be mentioned that leakage occurred at one stage, by which perhaps 200 c.c. of air entered the apparatus ; and, besides, the nitrogen was collected over water from which it doubtless acquired some argon. Quantitative negative experiments of this nature are exceedingly difficult, and require a long time to carry them to a successful conclusion.

### VIII. *Separation of Argon on a Large Scale.*

To prepare argon on a large scale, air is freed from oxygen by means of red-hot copper. The residue is then passed from a gas-holder through a combustion-tube, heated in a furnace, and containing copper, in order to remove all traces of oxygen ; the issuing gas is then dried by passage over soda-lime and phosphorus pentoxide, after passage through a small ∪ tube containing sulphuric acid, to indicate the rate of flow. It then enters a combustion-tube packed tightly with magnesium turnings, and heated to redness in a second furnace. From this tube it passes through a second index-tube, and enters a small gas-holder capable of containing 3 or 4 litres. A single tube of magnesium will absorb from 7 to 8 litres of nitrogen. The temperature must be nearly that of the fusion of the glass, and the current of gas must be carefully regulated, else the heat developed by the union of the magnesium with nitrogen will fuse the tube.

Having collected the residue from 100 or 150 litres of atmospheric nitrogen, which may amount to 4 or 5 litres, it is transferred to a small gas-holder connected with an apparatus, whereby, by means of a species of a self-acting Sprengel's pump, the gas is caused to circulate through a tube half filled with copper and half with copper oxide ; it then traverses a tube half filled with soda-lime and half with phosphorus pentoxide ; it then passes a reservoir of about 300 c.c. capacity, from which, by raising a mercury reservoir, it can be expelled into a small gas-holder. Next it passes through a tube containing magnesium turnings heated to bright redness. The gas

is thus freed from any possible contamination with oxygen, hydrogen, or hydrocarbons, and nitrogen is gradually absorbed.  As the amount of gas in the tubes and reservoir diminishes in volume, it draws supplies from the gas-holder, and, finally, the circulating system is full of argon in a pure state.  The circulating system of tubes is connected with a mercury pump, so that, in changing the magnesium tube, no gas may be lost.  Before ceasing to heat the magnesium tube the system is pumped empty, and the collected gas is restored to the gas-holder ; finally, all the argon is transferred from the mercury reservoir to the second small gas-holder, which should preferably be filled with water saturated with argon, so as to prevent contamination from oxygen or nitrogen ; or, if preferred, a mercury gas-holder may be employed.  The complete removal of nitrogen from argon is very slow towards the end, but circulation for a couple of days usually effects it.

The principal objection to the oxygen method of isolating argon, as hitherto described, is the extreme slowness of the operation.  In extending the scale we had the great advantage of the advice of Mr. Crookes, who not long since 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.*  The plant consists of a De Meritens alternator, actuated by a gas engine, and the currents are tranformed to a high potential by means of a Ruhmkorff or other suitable induction coil.  The highest rate of absorption of the mixed gases yet attained is 3 litres per hour, about 3000 times that of Cavendish.  It is necessary to keep the apparatus cool, and from this and other causes a good many difficulties have been encountered.

In one experiment of this kind, the total air led in after seven days' working, amounted to 7925 c.c., and of oxygen (prepared from chlorate of potash), 9137 c.c.  On the eighth and ninth days oxygen alone was added, of which about 500 c.c. was consumed, while there remained about 700 c.c. in the flask.  Hence the proportion in which the air and oxygen combined was as 79 : 96.  The progress of the removal of the nitrogen was examined from time to time with the spectroscope, and became ultimately very slow.  At last the yellow line disappeared, the contraction having apparently stopped for two hours.  It is worthy of notice that with the removal of the nitrogen, the arc discharge changes greatly in appearance, becoming narrower and blue rather than greenish in colour.

The final treatment of the residual 700 c.c. of gas was on the model of the small scale operations already described.  Oxygen or hydrogen could be supplied at pleasure from an electrolytic apparatus, but in no way could the volume be reduced below 65 c.c.  This residue

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

refused oxidation, and showed no trace of the yellow line of nitrogen, even under favourable conditions.

When the gas stood for some days over water, the nitrogen line reasserted itself in the spectrum, and many hours' sparking with a little oxygen was required again to get rid of it. Intentional additions of air to gas free from nitrogen showed 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 connected to the secondary terminals.

### IX. *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 already recorded 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,
$\alpha$ = 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 $\alpha$ are both small, but they are known with fair accuracy. From the data already given

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

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 $20 \cdot 6$.

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 employed for other gases. A *mixture* of about 400 c.c. of argon with pure oxygen, however, gave the weight $2 \cdot 7315$, $0 \cdot 1045$ in excess of the weight of oxygen, viz., $2 \cdot 6270$. Thus, if $\alpha$ 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 $\alpha$, 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 $3\cdot 193$, so that, if $O_2 = 16$, the density of the gas would be $19\cdot 45$. An allowance for residual nitrogen, still visible in the gas before admixture of oxygen, raises this number to $19\cdot 7$, which may be taken as the density of pure argon resulting from this determination.

## X. *Density of Argon prepared by means of Magnesium.*

The density of the original sample of argon prepared has already been mentioned. It was $19\cdot 09$; and, after sparking with oxygen, it was calculated to be $20\cdot 0$. The most reliable results of a number of determinations give it as $19\cdot 90$. The difficulty in accurately determining the density is to make sure that all nitrogen has been removed. The sample of density $19\cdot 90$ showed no spectrum of nitrogen when examined in a vacuum tube. It is right, however, to remark that the highest density registered was $20\cdot 38$. But there is some reason here to distrust the weighing of the vacuous globe.

## XI. *Spectrum of Argon.*

The spectrum of argon, seen in a vacuum tube of about 3 mm. 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 will give a full account of the spectrum in a separate communication, has kindly furnished us with the accurate wavelengths of these lines, as well as of some others next to be described; they are respectively $696\cdot 56$ and $705\cdot 64$, $10^{-6}$ mm.

Besides these red lines, a bright yellow line, more refrangible than the sodium line, occurs at $603\cdot 84$. A group of five bright green lines occurs next, besides a number of less intensity. Of the group of five, the second, which is perhaps the most brilliant, has the wavelength $561\cdot 00$. There is next a blue or blue-violet line of wavelength $470\cdot 2$; 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 $420\cdot 0$.

Unfortunately, the red lines, which are not to be mistaken for those of any other substance, are not easily seen when a jar discharge is passed through argon at atmospheric pressure, unless a large jar and a very powerful current be employed. 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 charac- |
| 473·53 . . . . . . . . . . . . . . | teristic triplet. |
| 472·56 . . . . . . . . . . . . . . | |

It is necessary to anticipitate Mr. Crookes' 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 pole 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. 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." 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.

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

Professor Schuster also has found the principal lines identical in the spectra of the two gases, as observed by the jar discharge at atmospheric pressure.

* 'Proc. Phys. Soc.,' 1893, p. 147.

### XII.  *Solubility of Argon in Water.*

Determinations of the solubility in water of argon, prepared by sparking, gave 3·94 volumes per 100 of water at 12°.   The solubility of gas prepared by means of magnesium was found to be 4·05 volumes per 100 at 13·9°.   The gas is therefore about 2½ times as soluble as nitrogen, and possesses approximately the same solubility as oxygen.

The fact that argon 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.   " Nitrogen " prepared from the dissolved gases of water supplied from a rain-water cistern was weighed upon two occasions.   The weights, corresponding to those recorded in § I, were 2·3221 and 2·3227, showing an excess of 24 milligrams above the weight of true nitrogen.   Since the corresponding excess for " atmospheric nitrogen " is 11 milligrams, we conclude that the water " nitrogen " is relatively more than twice as rich in argon.

On the other hand, gas evolved from the hot spring at Bath, and collected for us by Dr. A. Richardson, gave a residue after removal of oxygen and carbonic acid, whose weight was only about midway between that of true and atmospheric nitrogen.

### XIII.  *Behaviour at Low Temperatures.*[*]

Preliminary experiments, carried out to liquefy argon at a pressure of about 100 atmospheres, and at a temperature of −90°, failed.   No appearance of liquefaction could be observed.

Professor Charles Olszewski, of Cracow, the well-known authority on the constants of liquefied gases at low temperatures, kindly offered to make experiments on the liquefaction of argon.   His results are embodied in a separate communication, but it is allowable to state here that the gas has a lower critical temperature (−121°) and a lower boiling point (−187°) than oxygen, and that he has succeeded in solidifying argon to white crystals, melting at −189·6°.   The density of the liquid is approximately 1·5, that of oxygen being 1·124, and of nitrogen 0·885.   The sample of gas he experimented with was exceptionally pure, and had been prepared by help of magnesium.   It showed no trace of nitrogen when examined in a vacuum tube.

### XIV.  *Ratio of Specific Heats.*

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 in a gas, the

[*] The arrangements for the experiments upon this branch of the subject were left entirely in Professor Ramsay's hands.

ratio of specific heat at constant pressure to that at constant volume can be deduced by means of the equation

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

when $n$ is the frequency, $\lambda$ 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 means of the proportion

$$\lambda^2 d : \lambda'^2 d' :: 1\cdot41 : x,$$

where, for example, $\lambda$ and $d$ refer to air, of which the ratio is $1\cdot41$, according to observations by Röntgen, Wüllner, Kayser, and Jamin and Richard.

Two completely different series of observations, one in a tube of about 2 mm. diameter, and one in one of 8 mm., made with entirely different samples of gas, gave the first, $1\cdot65$ as the ratio, and, the second, $1\cdot61$.

Experiments made with the first tube, to test the accuracy of its working, gave for carbon dioxide the ratio $1\cdot276$, instead of $1\cdot288$, the mean of all previous determinations; and the half wave-length of sound in hydrogen was found to be $73\cdot6$, instead of $74\cdot5$, the mean of those previously found. The ratio of the specific heats of hydrogen found was $1\cdot39$, instead of $1\cdot402$.

There can be no doubt, therefore, that argon gives practically the ratio of specific heats, viz., $1\cdot66$, proper to a gas in which all the energy is translational. The only other gas which has been found to behave similarly is mercury gas, at a high temperature.*

## XV. Attempts to induce Chemical Combination.

Many attempts to induce argon to combine will be described in full in the complete paper. Suffice it to say here, that all such attempts have as yet proved abortive. Argon does not combine with oxygen in presence of alkali under the influence of the electric discharge, nor with hydrogen in presence of acid or alkali also when sparked; nor with chlorine, dry or moist, when sparked; nor with phosphorus at a bright-red heat, nor with sulphur at bright redness. Tellurium may be distilled in a current of the gas; so may sodium and potassium, their metallic lustre remaining unchanged. It is unab-

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

sorbed by passing it over fused red-hot caustic soda, or soda-lime heated to bright redness ; it passes unaffected over fused and bright red-hot potassium nitrate ; and red-hot sodium peroxide does not combine with it. Persulphides of sodium and calcium are also without action at a red heat. Platinum black does not absorb it, nor does platinum sponge, and wet oxidising and chlorinating agents, such as nitro-hydrochloric acid, bromine water, bromine and alkali, and hydrochloric acid and potassium permanganate, are entirely without action. Experiments with fluorine are in contemplation, but the difficulty is great ; and an attempt will be made to produce a carbon arc in the gas. Mixtures of sodium and silica and of sodium and boracic anhydride are also without action, hence it appears to resist attack by nascent silicon and by nascent boron.

## XVI. *General Conclusions.*

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

The presence of argon in the atmosphere is proved by many lines of evidence. The higher density of "atmospheric nitrogen," and the uniformity in the density of samples of chemical nitrogen prepared from different compounds, lead to the conclusion that the cause of the anomaly is the presence of a heavy gas in air. If that gas possess the density 20 compared with hydrogen, " atmospheric nitrogen" should contain of it approximately 1 per cent. This is, in fact, found to be the case. Moreover, as nitrogen is removed from air by means of red-hot magnesium, the density of the remaining gas rises proportionately to the concentration of the heavier constituent.

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. This has been proved by its increase in density.

Third. 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 the removal of the oxygen, exceed that of "atmospheric nitrogen." Experiment has shown that the density is considerably increased.

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

x 2

appears probable, argon be an element, or a mixture of elements, its manufacture would mean its separation from one of the substances employed. The gas which can be removed from red-hot magnesium in a vacuum has been found to be wholly hydrogen. Nitrogen from chemical sources has been practically all absorbed by magnesium, and also when sparked in presence of oxygen; hence argon cannot have resulted from the decomposition of nitrogen. That it is not produced from oxygen is sufficiently borne out by its preparation by means of magnesium.

Other arguments could be adduced, but the above are sufficient to justify the conclusion that argon is present in the atmosphere.

The identity of the leading lines in the spectrum, the similar solubility and the similar density, appear to prove the identity of the argon prepared by both processes.

That argon is an element, or a mixture of elements, may be inferred from the observations of § XIV. 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 (§ XIV), 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.

From Avogadro's law, the density of a gas is half its molecular weight; and as the density of argon is approximately 20, hence its molecular weight must be 40. But its molecule is identical with its atom; hence its atomic weight, or, if it be a mixture, the mean of the atomic weights of that mixture, taken for the proportion in which they are present, must be 40.

There is evidence both for and against the hypothesis that argon is a mixture: for, owing to Mr. Crookes' 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.
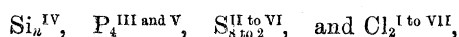
For the present, however, the balance of evidence seems to point to simplicity. We have therefore to discuss the relations to other elements of an element of atomic weight 40. We inclined for long to the view that argon was possibly one or more than one of the elements which might be expected to follow 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 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

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

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 in-different 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 com-parative molecular simplicity to the latter. Argon, with its com-paratively 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, who have materially assisted us in the prosecution of this research.

## Addendum by Professor RAMSAY, March 20, 1895.

Further determinations have been made of the density of argon prepared by means of magnesium. The mean result of six very concordant weighings of different samples, in which every care was taken in each case to circulate the argon over magnesium for hours after all contraction had ceased, gave the density 19·90.

The value of R in the gas-equation $R = pv/T$ has been carefully determined for argon, at temperatures determined by means of a thermometer filled with pure hydrogen. I have found that the value of R remains practically constant between $-87°$ and $+248°$; the greatest difference between the extreme values of R amounts to only 0·3 per cent. Argon, therefore, behaves as a " perfect " gas, and shows no sign of association on cooling, nor of dissociation on heating.

The ratio of the specific heat at constant volume to that at con-stant pressure has been reinvestigated ; the mean of four very concord-ant determinations with distinct samples of argon is 1·645.

The molecular weight of argon is therefore 39·8, and the same number expresses its atomic weight, unless it be a mixture of two elements, or of mono- and diatomic molecules of the same element. The ratio of specific heats might support the last supposition; but the thermal behaviour of the gas lends no support to this view.

## II. "On the Spectra of Argon." By WILLIAM CROOKES, F.R.S., &c. Received January 26, 1895.

(Abstract.)

Through the kindness of Lord Rayleigh and Professor Ramsay I have been enabled to examine the spectrum of this gas in a very accurate spectroscope, and also to take photographs of its spectra in a spectrograph fitted with a complete quartz train.

Argon resembles nitrogen in that it gives two distinct spectra according to the strength of the induction current employed. But while the two spectra of nitrogen are different in character, one showing fluted bands and the other sharp lines, the argon spectra both consist of sharp lines. It is, however, very difficult to get argon so free from nitrogen that it will not at first show the nitrogen flutings superposed on its own special system of lines. I have used argon prepared by Lord Rayleigh, Professor Ramsay, and myself, and, however free it was supposed to be from nitrogen, I could always detect the nitrogen bands in its spectrum. These, however, disappear when the induction spark is passed through the tube for some time, varying from a few minutes to a few hours. The vacuum tubes best adapted for showing the spectra are of the ordinary Plücker form, having a capillary tube in the middle. For photographing the higher rays which are cut off by glass I have used a similar tube, "end on," having a quartz window at one end.

The pressure of argon giving the greatest luminosity and most brilliant spectrum is 3 mm.

If the pressure is further reduced, and a Leyden jar intercalated in the circuit, the colour of the luminous discharge changes from red to a rich steel blue, and the spectrum shows an almost entirely different set of lines.

I have taken photographs of the two spectra of argon partly superposed. In this way their dissimilarity is readily seen.* In the spectrum of the blue glow I have counted 119 lines, and in that of the red glow 80 lines, making 199 in all. Of these 26 appear to be common to both spectra.

I have said that the residual nitrogen is removed by sparking the

* Photographs of the different spectra of argon, and other gaseous spectra for comparison, were projected on the screen.