"The Homogeneity of Helium and of Argon." By WILLIAM RAMSAY, Ph.D., F.R.S., and J. NORMAN COLLIE, Ph.D., F.R.S. Received July 21, 1896.

Preliminary.

It was pointed out by Lord Rayleigh and one of the authors that it is a legitimate conclusion to draw, from the found ratio between its specific heat at constant pressure and that at constant volume, that argon is a monatomic element ('Phil. Trans.,' 1895, A, p. 235). A similar deduction can be drawn regarding helium ('Chem. Soc. Trans.,' 1895, p. 699). And as the molecular weight of hydrogen is accepted as twice its atomic weight, and as the density of helium is approximately 2, and that of argon approximately 20, the molecular weights of these elements are approximately 4 and 40 respectively. If, however, the molecule is identical with the atom, then the atomic weights must also necessarily be 4 and 40.

But argon, with an atomic weight of 40, finds no place in the periodic table of the elements, if, as is usual, it is contended that the elements must necessarily follow each other in the numerical order of their atomic weights.

Certain suppositions may be made which would obviate this difficulty. First, the evidence from the ratio of the specific heats may lead to a false conclusion. But it is inconceivable that any structure, except one of the simplest kind, should transform all energy communicated to it as heat, into kinetic energy of translation. Still, before a final decision on this point is arrived at, it would be well to actually determine the specific heat of argon, and this will shortly be done. It may, however, be mentioned, that preliminary experiments have shown it to be much lower than that of hydrogen, air, or carbon dioxide, volume for volume.

Second, helium and argon may consist of a mixture of monatomic with diatomic molecules. The perfectly normal expansion of these gases appears to negative this supposition ('Phil. Trans.,' *loc. cit.*, p. 239, and 'Roy. Soc. Proc.,' vol. 59, p. 60). Even at a temperature of $-88°$ there appears to be no marked tendency towards association. It is true that the ratios of the specific heats do not quite reach the theoretical number 1·667. That found for helium was 1·652, and that for argon 1·659, with the most carefully purified samples. Assuming (what there seems good ground to doubt) that the last decimal place may be trusted, helium can be calculated to contain nearly 7 per cent. of diatomic molecules, and argon rather more than 3 per cent. If this calculation be permitted, the atomic weight of helium would become 4·02, taking its found density at

2·15, and of argon 38·62. This would place argon below potassium, the atomic weight of which is 39·1. However, it must be acknowledged that such refinements in calculation are far from trustworthy.

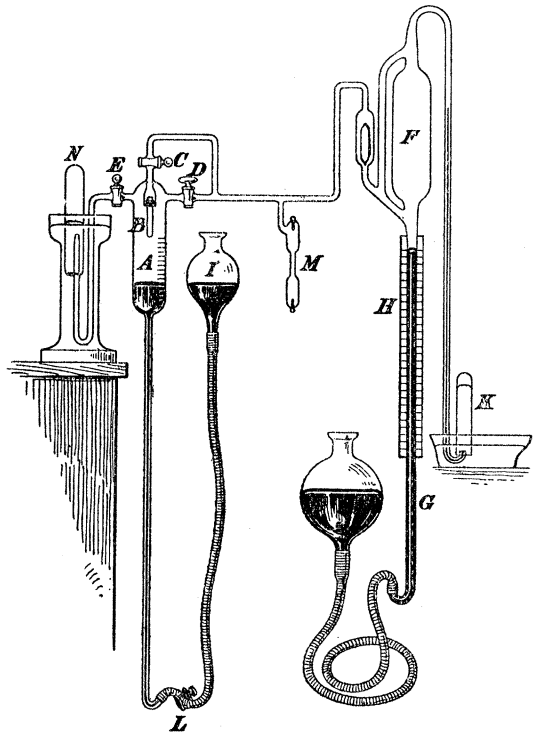
Third, helium and argon may each consist of a mixture of two or more elements. This view has been expressed with regard to helium by Professors Runge and Paschen ('Sitzungsber. d. Akad. d. Wissensch.,' Berlin, 1895, pp. 639 and 759), on the ground that the lines of its spectrum can be shown to belong to two distinct series. The question whether argon is a mixture or not was discussed in the memoir by Lord Rayleigh and one of the authors (*loc. cit.*, p. 236). It is with this possibility that the present communication has to deal.

Two methods suggest themselves as suitable in order to ascertain whether argon and helium are mixtures of two or more elements, or are single elements. The first is fractional solution in water; the second fractional diffusion. The second method is obviously the better calculated to yield the desired data; for if these gases contain constituents of different density, diffusion is an infallible means of separating them.

Description of Diffusion Apparatus.

After a number of trials, the stem of an ordinary tobacco-pipe was found to yield the best results. Plaster of Paris is too porous, and various forms of graphite tried did not effect so rapid a separation of two known gases as unglazed clay. In fact, nothing could have been more satisfactory than this apparatus.

It consists of a reservoir for the gas, A, into which projects a piece of the stem of a tobacco-pipe, B, sealed at the lower end in the flame of an oxy-hydrogen blowpipe. When the stop-cock C is open, and D and E shut, the gas in A must pass through the pipe-clay tube on its way to the reservoir of the pump F. The fall of the mercury in the tube G, read on the scale H, is timed, about 8 cm. fall being taken as sufficient for the purpose. The mercury rises in A, and falls in the reservoir I during the diffusion. When the experiment is finished, the gas is pumped out of the reservoir F, and collected in tubes similar to that depicted at K, and stored in a frame resembling a miniature umbrella-stand. The stop-cock D is then opened, and the clip L is shut, and the less diffusible portion of the gas is pumped out and collected in other tubes, and set apart. The purity of the gas is ascertained by means of the vacuum tube M. After all gas has been removed, the stop-cocks C and D are shut; a new charge of gas is introduced at N, the stop-cock E being opened, and the operation repeated. After a sufficient amount of the first diffusate has been collected, it is again introduced into the reservoir A, and the process repeated.



When towards the end only a small amount of gas is available, the process may be modified by raising the reservoir I, and so diminishing the volume of A. The clip L is then closed, and the gas is allowed to diffuse as before, but the volume in A is kept constant. The rate of diffusion can be compared with that of hydrogen under precisely similar circumstances.

In all the experiments the temperature did not alter by more than a degree or two; as the object was to effect a separation, and not to make accurate determinations of the rates of diffusion of gases, careful regulation of temperature was unnecessary.

Determination of the Ratios of Diffusion of Gases of known Purity.

(*a*) *Hydrogen.*—The time required for the column of mercury in H to sink through 8 centimetres, starting always from the same level, was found in three experiments to be (1) 433″, (2) 420″, and (3) 437″; the mean is 430″. The average rate per millimetre is 5·37″.

(*b*) *Oxygen.*—The time which pure oxygen, made from permanga-

nate, took to diffuse to the same extent was 1719″, giving an average rate per millimetre of 21·49″.

(*c*) *Acetylene.*—The gas was prepared from pure calcium carbide by the action of water. It dissolved completely in alcohol. The time required for diffusion was 1550″, giving a rate per millimetre of 19·37″.

Assuming the times for the diffusion of these gases to be proportional to the square roots of their densities, we have—

$$\text{For oxygen } \frac{5{\cdot}37'' \times \sqrt{16}}{\sqrt{1{\cdot}0082}} = 21{\cdot}39''. \quad \text{Found } 21{\cdot}49''.$$

$$\text{For acetylene } \frac{5{\cdot}37'' \times \sqrt{13{\cdot}008}}{\sqrt{1{\cdot}0082}} = 19{\cdot}29''. \quad \text{Found } 19{\cdot}37''.$$

This process may therefore be trusted to give fairly accurate results when applied to test the rates of diffusion of gases of known purity.

The Separation of a Mixture of Gases.

To ascertain whether a separation could be easily effected, experiments were made (*a*) on a mixture of oxygen and carbon dioxide, and (*b*) on a mixture of hydrogen and helium.

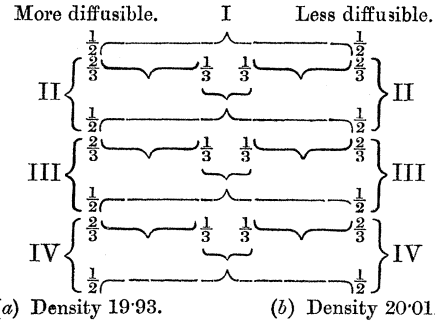
(*a*) *Oxygen and Carbon Dioxide.*—The original mixture contained 36 per cent. by volume of carbon dioxide. It was split into two approximately equal portions; each of these was again split into two. The most diffusible part contained 30·2 per cent. of carbon dioxide, and the least diffusible part 41·0 per cent.

(*b*) *Hydrogen and Helium.*—The original mixture contained 50 per cent. of each gas, and its volume was 38 c.c. 19 c.c. were diffused; this was again halved, 9·5 c.c. being passed through the pipe; and finally another diffusion of the 9·5 c.c. yielded 4·12 c.c. of mixed gases. The hydrogen was removed by explosion with oxygen. This mixture now consisted of 67 per cent. of hydrogen and 33 per cent. of helium.

From these experiments it is seen that a partial separation of such gases is easily carried out.

The Fractional Diffusion of Argon.

Four hundred c.c. of argon, newly circulated over red-hot magnesium until spectroscopic traces of nitrogen were carefully removed, was diffused according to the subjoined scheme:—



(*a*) Density 19·93. (*b*) Density 20·01.

The densities were determined by weighing.

These numbers show that no important separation has been effected. The difference in density of the two portions may possibly be attributed to experimental error. When the density of the heavier portion was taken the weather was damp, and we have found it difficult to obtain concordant results under such circumstances, owing doubtless to the uneven deposition of moisture on the surfaces of the bulb and its counterpoise. But as it stands, the difference is an extremely minute one, and it may, we think, be taken that any separation of argon, if effected at all, is very imperfect.

The Fractional Diffusion of Helium.

Two hundred c.c. of helium from fergusonite of density 2·13 were separated into two nearly equal portions by diffusion. The rate of diffusion was 7·14″ per millimetre as a mean of two experiments, giving 7·13″ and 7·15″ respectively. The most diffusible portion of this gas gave the rate 7·12″ per millimetre. The more diffusible half of this gas had the rate 7·48″, and the least diffusible of the remainder 7·38″, the temperature being lower. A second specimen of helium from mixed sources, samarskite, fergusonite, bröggerite, &c., which showed the nitrogen spectrum strongly, gave a rate for the first portion of 8·29″. This half on rediffusion had the rate 7·64″, and the residue of 8·39″, showing that a separation was being effected. The heavier residue of the remainder from that portion which showed the rate 8·39″ was too small to make it possible to diffuse it by the usual method. A second method was therefore resorted to, and it was directly compared with hydrogen under the same circumstances. While hydrogen took 12·14″ per millimetre, the residue took 21·00″, and calculating its density from these rates, we have—

$$\frac{21{\cdot}00'')^2 \times 1{\cdot}0082}{(12{\cdot}14'')^2} = 3{\cdot}02.$$

This would correspond, if it be granted that the impurity is nitrogen, to a percentage of 8·5 of that gas. This residue showed a

strong nitrogen spectrum; and the nitrogen was removed by sparking with oxygen in presence of soda, until the spectrum attested its absence. (It will be remembered that 0·01 per cent. of nitrogen is still visible under moderate pressures, 'Roy. Soc. Proc.,' vol. 59, p. 265.) The rate was again measured against that of hydrogen under precisely similar conditions, and it was found that while hydrogen took 20·00″ for diffusion, this specimen of helium took 28·28″. And calculation shows its density to be now 2·015.

These experiments were sufficient to show, we think, that while it is possible to separate nitrogen from helium, even although the former is present in only small amount, we had not succeeded in separating helium itself into two portions of different densities. If, then, helium were a mixture, its constitutents must possess nearly the same density. In no case was any alteration of the spectrum to be noticed; the diffusate and the residue were similar, and showed all the well known lines of helium with the usual intensity.

But it was deemed advisable, in view of the importance of the matter, to undertake a much more elaborate set of experiments. The helium was carefully purified from hydrogen and nitrogen by circulation over magnesium, copper oxide, phosphorus pentoxide, and soda lime, until a small quantity admitted into a vacuum tube in connection with the circulating apparatus showed no spectrum either of hydrogen or nitrogen, even at a comparatively high pressure, when these gases are more easily detected. The helium was then fractionated in a manner exactly similar to that shown in the graphic scheme for argon (p. 210). The rates of diffusion of the two samples of gas were then measured.

More diffusible portion—	
Time of diffusion reduced to 0°	662·5″
Hydrogen	492·3″
Density, calculated from rate	1·826
Less diffusible portion—	
Time of diffusion	654·9″
Hydrogen, at same temperature	484·4″
Density, calculated from rate	1·842

The density of hydrogen was taken as 1·0082, on the standard, oxygen = 16.

These samples were next weighed.

More diffusible portion—	
Volume of globe	162·843 c.c.
Pressure at filling	668·5 mm.
Temperature	19·20°
Weight	0·02450 gram
Density	2·049

Less diffusible portion—

Volume of globe.....	162·843 c.c.
Pressure at filling	663·8 mm.
Temperature	19·93°
Weight	0·02902 gram
Density.....	2·452

The less diffusible portion was next subjected to the process of removing nine-tenths, the remaining tenth being collected apart. This process was repeated three times, so that any portion of gas less diffusible than the main bulk should thus be left as a residue. From the more diffusible portion nine-tenths was also diffused out. The more diffusible portions were then mixed, and the density was again determined.

Volume of globe.....	162·843 c.c.
Pressure at filling	765·7 mm.
Temperature	20·98°
Weight	0·02801 gram
Density	2·057

This number is practically identical with that previously obtained, viz., 2·049.

It was of interest to follow the less diffusible gas, so as to ascertain what impurity caused its higher density. Another set of fractionations was therefore carried out, and after five separate processes, in each of which a residue was left, and that residue further diffused, so as to separate all light gas as completely as possible, a few c.c. of gas were collected, in which the spectrum of argon was strong. Now we are certain that at no stage in the operations was any considerable quantity of air admitted by leakage. It may safely be said that the total amount of air could never have exceeded 5 c.c. And inasmuch as the density of samples of helium from various sources, which had undergone very little handling, differed by small amounts, varying between 2·114 and 2·181, this must be ascribed to contamination with argon, contained in the mineral from which the helium had been obtained. Every effort was made to detect any unknown lines in the spectrum of the residue, but in vain. With the jar and spark-gap, the blue spectrum of argon was visible, and was compared with that from a standard tube.

If thus the increased density is due to argon, it is possible to calculate the proportion of the latter; first, in the lightest gas of density 2·117 found in samarskite; second, in the residue in which the argon had been concentrated, possessing the density 2·452, on the assumption that helium possesses the density 2·042. The first must contain 0·42 per cent. of argon; the second, 2·28 per cent.

The rate of diffusion of the gas of density 2·057 was determined finally, so as to afford a check on its density. It took 657·9″ for a quantity to diffuse; while the same volume of hydrogen under precisely similar circumstances took 492·3″. Reducing these numbers to density, if hydrogen be taken as 1·0082, the helium possesses the density 1·801, which compares very favourably with the number already found, 1·826.

As a final check on these results, a sample of helium from an entirely different source, samarskite, was so diffused, that first nine-tenths were removed by diffusion; from the residue nine-tenths was again removed, and the process was repeated a third time. The more diffusible portion was tested as regards rate; while hydrogen took 492·3″ to diffuse, this sample took 652·6″. Stated as density, the number is 1·771.

The actual density was next determined, with the following result:—

Volume of globe.....	162·843 c.c.
Pressure at filling	691·6 mm.
Temperature	19·85°
Weight	0·02567 gram
Density	2·080

This number closely coincides with the density of the previous specimen, freed from argon by diffusion; and in this case it must be remembered, no systematic process for separating two possible constituents was carried out, but the heavier portion only was removed. The heavier gas separated by diffusion was examined for argon, and it was possible to see the green group of five lines, but not the red lines. And with a jar and spark-gap, argon could just be detected.

The rate of diffusion of this gas, which, stated as density, gives the number 1·8, differs from the density determined by weighing, viz., 2·08, or thereabouts. This might be caused (1) by a lighter portion passing over first during diffusion, leaving a heavier portion behind; or (2) by the hypothesis that the rate of diffusion of helium is abnormal; and helium has already shown such very remarkable properties in relation to refractivity for light, and conductivity for electricity, that the hypothesis is not unwarrantable. The first supposition, however, is the more probable, and was put to the test in the following manner.

A smaller apparatus was made for measuring the rate of diffusion of 10 to 20 c.c. of gas; and the rates of the sample of density 2·08, and of the less diffusible residues from this sample were determined. Both the hydrogen and the helium were carefully measured and diffused under precisely similar conditions. While the hydrogen took 181″ to diffuse, the helium of density 2·08 took 246·6″, implying a

density of 1·871; and the residue diffused in 266·6″, which corresponds to a density of 2·187. In each of these experiments about half the helium passed through the porous plug.

The denser portion of this gas was again diffused five times, lighter portions being removed. This corresponds to a residue of 30 c.c. from 400 c.c. of the original gas. The rate of diffusion of this sample compared with that of hydrogen was almost identical with the last, namely 208″ to 143″, and corresponds to a density of 2·133. The gas is therefore not increased in density by this process.

The lighter gas was submitted to a similar fractionation, and the ratio of its diffusion-rate to that of hydrogen was 246·75″ to 181·0″, as a mean of several closely concordant experiments. This corresponds to a density of 1·874. We have accordingly:—

	Density.
"Heavy" portion	2·133
"Light" portion	1·874

Not content with this, we pushed fractionation still further; the helium was divided into seven portions (by fractionation) and then submitted to methodical fractional diffusion, in which the heavier portions were transferred to the "denser" side, and the lighter portions to the "lighter" side. This process was repeated four times, and the end portions were each divided into two; the lighter portion of the "lighter" was collected separately, and its rate determined. It took 258·5″ to diffuse, compared with 189·5″ for an equal volume of hydrogen; its density calculated from these rates was 1·876. It is clear, therefore, that the limit has been reached in purifying the lighter portion by diffusion.

It should have been mentioned that the portion of 2·133 density as well as that of 1·874 density had been sparked with oxygen in presence of potash, and in a vacuum tube showed mere traces of hydrogen, every other gas being absent. The spectrum of hydrogen is still visible, even when 0·01 per cent. of that gas is present.

At various times during the attempt to separate helium, the spectrum has been carefully examined. *The very first* portions of the lightest gas gave an identical spectrum, seen with a hand-spectroscope, with *the very last* portions of the heaviest gas. Professor Ames, of the Johns Hopkins University, has however kindly undertaken to photograph the spectra using a dispersion-grating; so that if any difference can be detected, it will ere long be made known.

Lord Rayleigh was so kind as to measure the refractivity of these extreme portions of the fractionated gas. His process has been described in the 'Proceedings,' vol. 59, p. 202. For the sample of helium sent him in July, 1895, he found the number 0·146. The lighter portion of the fractionated gas of density 1·876 had a refrac-

tivity, compared with air as unity, of 0·1350; the heavier portion, of 0·1524. The ratio of these numbers is very nearly that between the densities of the gases, viz.:—

$$\frac{0{\cdot}1350}{0{\cdot}1524} = \frac{1{\cdot}876}{2{\cdot}118}, \text{ instead of } \frac{1{\cdot}876}{2{\cdot}133}.$$

Conclusion.

It must be remarked that the rate of diffusion of helium is too rapid for its density measured by weighing. There can be no doubt, we think, that the density of the lighter portion, instead of being 1·874, would be, if actually weighed, 2·05 or 2·08. And the heavier portion has doubtless a proportionately higher density. But, assuming that the densities calculated from the diffusion-rates are correct, the densities of the two gases, supposing that two exist, are 1·871. and 2·133, respectively.

Also, we must not omit to state that careful experiments were made with the more rapidly diffusing gas to prove that the first portions passing over did not diffuse at a more rapid rate than the later portions, no difference in diffusion rates, compared with those of hydrogen under the same circumstances having been detected.

That helium, then, consists of a mixture of two or more distinct gases is one solution of the problem, probably the one which recommends itself at first sight. But there is another, so revolutionary in its character that much must be done before it can be regarded as even worthy to be entertained. So much has, however, been lost to science by what may be termed scientific incredulity, that we regard it as well worth putting to a rigorous proof.

It is that a separation has been effected of light molecules from heavy molecules; that, in fact, a gas—in this case helium—is not constituted entirely of molecules of the same weight, but that the mixture of molecules which we term helium have weights which average 2·18, or whatever the density of ordinary undiffused helium may ultimately be found to be. The same supposition would, of course, be applicable to oxygen, nitrogen, or any gas. In separating such molecules from each other a practical limit must necessarily be reached, and this limit appears to have been reached with helium.

There is negative and positive probability in favour of this suggestion. First, no gas has been submitted to methodical diffusion with a view to effect such a separation, argon excepted; and here, too, there is faint evidence of a similar kind. It is proposed to carry out similar experiments with gases of undoubted homogeneity according to the usual views; and till such experiments have been made, it is impossible to decide the point definitely.

Second, Mr. E. C. C. Baly's experiments on oxygen appear to

point to a similar conclusion; although no great alteration in density has been produced, yet there is a sign that a kind of separation is being effected electrically. There is also in favour of the supposition the unlikelihood that two or more gases, so like one another as the constituents of helium, should exist with densities so near each other; and the probability that some separation should have been detected by aid of the spectroscope.

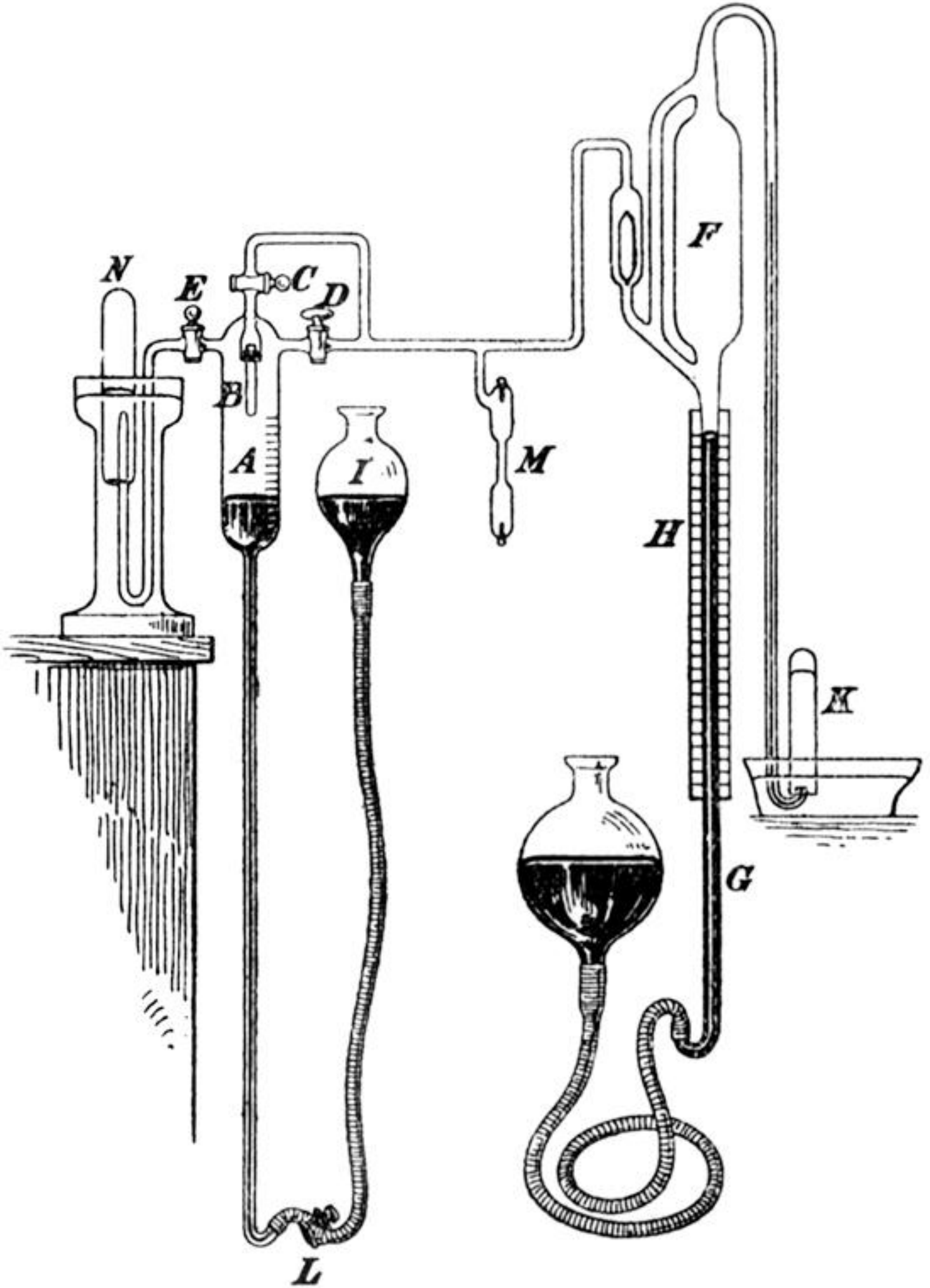
Lastly, the refractivities of both gases, if there be two, appear to be equally abnormal; now, different gases have different refractivities in no known relation to their densities, as, for example, hydrogen 0·5, oxygen nearly 1. But the refractivities of the different portions of helium are proportional to their densities; a statement which is true of any one gas, inasmuch as refractivity is directly proportional to pressure, *i.e.*, mass in unit volume. The refractivity of helium, also, is so small that it totally differs in this respect, as, indeed, it does in most of its physical properties from every other gas, and it is moreover a monatomic gas. It is therefore permissible to seek for an explanation of its remarkable properties in framing any hypothesis which admits of being put to the test.

"On the Spectrum of Cyanogen as produced and modified by Spark Discharges." By W. N. Hartley, F.R.S., Royal College of Science, Dublin. Received July 13, 1896.

The Production of Cyanogen in the Electric Arc.—The very careful and numerous experiments of Liveing and Dewar* have very generally been accepted as affording evidence sufficient to establish the existence of an emission spectrum of cyanogen as distinct from that of carbon in the electric arc. Kayser and Runge,† though at first disinclined to accept such a conclusion, obtained additional evidence by experimenting with the arc in air, and in carbon dioxide. They found that the ordinary carbon spectrum and that of cyanogen appeared with rapidity alternately in the arc in air, though there could be no difference in temperature sufficient to account for the production of two different carbon spectra. With the poles immersed in carbon dioxide no such changes were seen, the carbon spectrum alone being visible, which evidence led them to concur in the views of Liveing and Dewar. The chief evidence of the existence of a cyanogen spectrum rests on the fact that this substance is actually synthesised in the arc when nitrogen is present, and because without

* 'Roy. Soc. Proc.,' vol. 30, pp. 152—162, 494—509: vol. 34, pp. 123—130 and pp. 418—429.

† "Ueber die Spectren der Elemente. Zweiter Abschnitt. Ueber die im galvanischen Lichtbogen auftretenden Bandenspectren der Kohle." 'Abh. K. Preuss. Ak. Wiss.,' 1889, p. 9.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