the problem. This function, as formed, is redundant (or, as Sylvester would say, "crude"), as containing terms which do not appertain to the enumeration, and it has been a principal object to obtain condensed or reduced generating functions. It was not difficult to conjecture that if the graphs have not more than two layers of nodes (*i.e.*, not more than two nodes along the axis of z, taken to be perpendicular to the plane of the paper), but be otherwise unrestricted, the reduced generating function is—

$$(1-x)^{-1}(1-x^2)^{-2}(1-x^3)^{-2}(1-x^4)^{-2}\ldots(1-x^5)^{-2}\ldots \text{ ad inf.}$$

Failure to establish this happily led me to send the corresponding crude generating function to Professor Forsyth. He furnished an ingenious solution, which is on the point of appearing in the 'Proceedings of the London Mathematical Society.'

Subsequent to this I obtained a proof, of quite a different character and without reference to the crude form, of the same theorem which will be found in this section.

Conjecturally, the G.F.'s, when the layers are restricted in number to 3, 4, ..., &c., are—

$$(1-x)^{-1}(1-x^2)^{-2}\{(1-x^3)(1-x^4)\ldots \text{ ad inf.}\}^{-3},$$

$$(1-x)^{-1}(1-x^2)^{-2}(1-x^3)^{-3}\{(1-x^4)(1-x^5)\ldots \text{ ad inf.}\}^{-4}, \text{ &c.,}$$

and when the graphs are quite unrestricted—

$$(1-x)^{-1}(1-x^2)^{-2}(1-x^3)^{-3}(1-x^4)^{-4}\ldots(1-x^5)^{-5}\ldots \text{ ad inf.}$$

Finally, a conjecture is made as to the form when the graphs are restricted in all these dimensions.

These conjectures are slowly being transformed into truths, and I trust to present them as such to the Royal Society as Part 2 of this memoir.

IV. "On some Physical Properties of Argon and Helium." By Lord Rayleigh, Sec. R.S. Received January 16, 1896.

Density of Argon.

In our original paper* are described determinations by Prof. Ramsay, of the density of argon prepared with the aid of magnesium. The volume actually weighed was 163 c.c., and the adopted mean result was 19·941, referred to $O_2 = 16$. At that time a satisfactory conclusion as to the density of argon prepared by the oxygen

* Rayleigh and Ramsay, 'Phil. Trans.,' vol. 186, A, pp. 221, 238, 1895.

method of Cavendish had not been reached, although a preliminary result (19·7) obtained from a mixture of argon and oxygen* went far to show that the densities of the gases prepared by the two methods were the same. In order further to test the identity of the gases, it was thought desirable to pursue the question of density; and I determined, as the event proved, somewhat rashly, to attempt large scale weighings of pure argon with the globe of 1800 c.c. capacity employed in former weighings of gases† which could be obtained in quantity.

The accumulation of the 3 litres of argon, required for convenient working, involved the absorption of some 300 litres of nitrogen, or about 800 litres of the mixture with oxygen. This was effected at the Royal Institution with the apparatus already described,‡ and which is capable of absorbing the mixture at the rate of about 7 litres per hour. The operations extended themselves over nearly three weeks, after which the residual gases amounting to about 10 litres, still containing oxygen with a considerable quantity of nitrogen, were removed to the country and transferred to a special apparatus where it could be prepared for weighing.

For this purpose the purifying vessel had to be arranged somewhat differently from that employed in the preliminary absorption of nitrogen. When the gas is withdrawn for weighing, the space left vacant must be filled up with liquid, and afterwards when the gas is brought back for repurification, the liquid must be removed. In order to effect this, the working vessel (Fig. 7)§ communicates by means of a siphon with a 10-litre "aspirating bottle," the ends of the siphon being situated in both cases near the bottom of the liquid. In this way the alkaline solution may be made to pass backwards and forwards, in correspondence with the desired displacements of gas.

There is, however, one objection to this arrangement which requires to be met. If the reserve alkali in the aspirating bottle were allowed to come into contact with air, it would inevitably dissolve nitrogen, and this nitrogen would be partially liberated again in the working vessel, and so render impossible a complete elimination of that gas from the mixture of argon and oxygen. By means of two more aspirating bottles an atmosphere of *oxygen* was maintained in the first bottle, and the outermost bottle, connected with the second by a rubber hose, gave the necessary control over the pressure.

Five glass tubes in all were carried through the large rubber cork by which the neck of the working vessel was closed. Two of these

* *Loc. cit.*, p. 221.

† 'Roy. Soc. Proc.,' February, 1888; February, 1892; March, 1893.

‡ 'Phil. Trans.,' *loc. cit.*, p. 219.

§ 'Phil. Trans.,' *loc. cit.*, p. 218.

convey the electrodes: one is the siphon for the supply of alkali, while the fourth and fifth are for the withdrawal and introduction of the gas, the former being bent up internally, so as to allow almost the whole of the gaseous contents to be removed. The fifth tube, by which the gas is returned, communicates with the fall-tube of the Töpler pump, provision being made for the overflow of mercury. In this way the gas, after weighing, could be returned to the working vessel at the same time that the globe was exhausted. It would be tedious to describe in detail the minor arrangements. Advantage was frequently taken of the fact that *oxygen* could always be added with impunity, its presence in the working vessel being a necessity in any case.

When the nitrogen had been so far removed that it was thought desirable to execute a weighing, the gas on its way to the globe had to be freed from oxygen and moisture. The purifying tubes contained copper and copper oxide maintained at a red heat, caustic soda, and phosphoric anhydride. In all other respects the arrangements were as described in the memoir on the densities of the principal gases,* the weighing globe being filled at 0°, and at the pressure of the manometer gauge.

The process of purification with the means at my command proved to be extremely slow. The gas contained more nitrogen than had been expected, and the contraction went on from day to day until I almost despaired of reaching a conclusion. But at last the visible contraction ceased, and soon afterwards the yellow line of nitrogen disappeared from the spectrum of the jar discharge.† After a little more sparking, a satisfactory weighing was obtained on May 22, 1895; but, in attempting to repeat, a breakage occurred, by which a litre of air entered, and the whole process of purification had to be re-commenced. The object in view was to effect, if possible, a *series* of weighings with intermediate sparkings, so as to obtain evidence that the purification had really reached a limit. The second attempt was scarcely more successful, another accident occurring when two weighings only had been completed. Ultimately a series of four weighings were successfully executed, from which a satisfactory conclusion can be arrived at.

* 'Roy. Soc. Proc.,' vol. 53, p. 134, 1893.

† Jan. 29.—When the argon is nearly pure, the arc discharge (no jar connected) assumes a peculiar purplish colour, quite distinct from the greenish hue apparent while the oxidation of nitrogen is in progress and from the sky blue observed when the residue consists mainly of oxygen.

May 22	3·2710	
June 4	3·2617	
June 7	3·2727	
June 13	3·2652	
June 18	3·2750	3·2746
June 25	3·2748	
July 2	3·2741	

The results here recorded are derived from the comparison of the weighings of the globe "full" with the mean of the preceding and following weighings "empty," and they are corrected for the errors of the weights and for the shrinkage of the globe when exhausted, as explained in former papers. In the last series, the experiment of June 13 gave a result already known to be too low. The gas was accordingly sparked for fourteen hours more. Between the weighings of June 18 and June 25 there was nine hours' sparking, and between those of June 25 and July 2 about eight hours' sparking. The mean of the last three, viz., 3·2746, is taken as the definitive result, and it is immediately comparable with 2·6276, the weight under similar circumstances of oxygen.* If we take $O_2 = 16$, we obtain for argon

19·940,

in very close agreement with Professor Ramsay's result.

The conclusion from the spectroscopic evidence that the gases isolated from the atmosphere by magnesium and by oxygen are essentially the same is thus confirmed.

The Refractivity of Argon and Helium.

The refractivity of argon was next investigated, in the hope that it might throw some light upon the character of the gas. For this purpose absolute measurements were not required. It sufficed to compare the pressures necessary in two columns of air and argon of equal lengths, in order to balance the retardations undergone by light in traversing them.

The arrangement was a modification of one investigated by Fraunhofer, depending upon the interference of light transmitted through two parallel vertical slits placed in front of the object glass of a telescope. If there be only one slit, and if the original source, either a distant point or a vertical line of light, be in focus, the field is of a certain width, due to "diffraction," and inversely as the width of the slit. If there be two equal parallel slits whose distance apart is a considerable multiple of the width of either, the

* 'Roy. Soc. Proc.,' vol. 53, p. 144, 1893.

field is traversed by bands of width inversely as the distance between the slits. If from any cause one of the portions of light be retarded relatively to the other, the bands are displaced in the usual manner, and can be brought back to the original position only by abolishing the relative retardation.

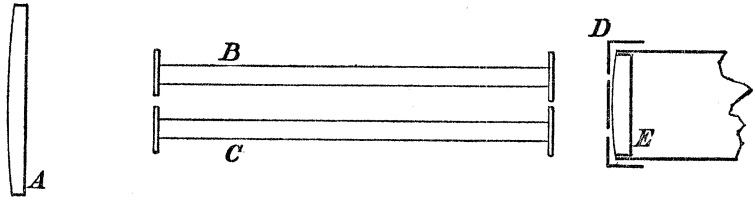
When the object is merely to see the interference bands in full perfection, the use of a telescope is not required. The function of the telescope is really to magnify the slit system,* and this is necessary when, as here, it is desired to operate separately upon the two portions of light. The apparatus is, however, extremely simple, the principal objection to it being the high magnifying power required, leading under ordinary arrangements to a great attenuation of light. I have found that this objection may be almost entirely overcome by the substitution of cylindrical lenses, magnifying in the horizontal direction only, for the spherical lenses of ordinary eye-pieces. For many purposes a single lens suffices, but it must be of high power. In the measurements about to be described most of the magnifying was done by a lens of home manufacture. It consisted simply of a round rod, about $\frac{1}{6}$ in. (4 mm.) in diameter, cut by Mr. Gordon from a piece of plate glass.† This could be used alone; but as at first it was thought necessary to have a web, serving as a fixed mark to which the bands could be referred, the rod was treated as the object-glass of a compound cylindrical microscope, the eye-piece being a commercial cylindrical lens of $1\frac{1}{4}$ in. (31 mm.) focus. Both lenses were mounted on adjustable stands, so that the cylindrical axes could be made accurately vertical, or, rather, accurately parallel to the length of the original slit. The light from an ordinary paraffin lamp now sufficed, although the magnification was such as to allow the error of setting to be less than 1/20 of a band interval. It is to be remembered that with this arrangement the various parts of the length of a band correspond, not to the various parts of the original slit, but rather to the various parts of the object-glass. This departure from the operation of a spherical eye-piece is an advantage, inasmuch as optical defects show themselves by deformation of the bands instead of by a more injurious encroachment upon the distinction between the dark and bright parts.

The collimating lens A (fig. 1) is situated 23 ft. (7 metres) from the source of light. B, C are the tubes, one containing dry air, the other the gas to be experimented upon. They are 1 ft. (30·5 cm.) long, and of $\frac{1}{2}$ in. (1·3 cm.) bore, and they are closed at the ends with small plates of parallel glass cut from the same strip. E is the object-glass of the telescope, about 3 in. (7·6 cm.) in diameter. It is fitted

* 'Brit. Assoc. Report,' 1893, p. 703.

† Preliminary experiments had been made with ordinary glass cane and with tubes charged with water.

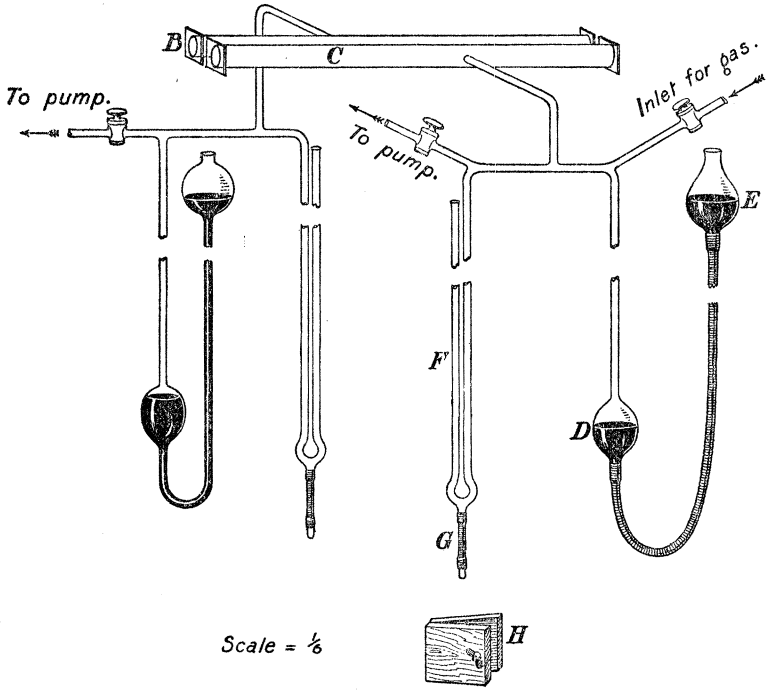
FIG. 1.



with a cap, D, perforated by two parallel slits. Each slit is $\frac{1}{4}$ in. (6 mm.) wide, and the distance between the middle lines of the slits is $1\frac{1}{2}$ in. (38 mm.).

The arrangements for charging the tubes and varying the pressures of the gases are sketched in fig. 2. A gas pipette, DE, communicates with the tube C, so that by motion of the reservoir E and consequent flow of mercury through the connecting hose, part of the gas may be transferred. The pressure was measured by a U-shaped manometer F, containing mercury. This was fitted below with a

FIG. 2.



short length of stout rubber tubing G, to which was applied a squeezer H. The object of this attachment was to cause a rise of mercury in both limbs immediately before a reading, and thus to avoid the capillary errors that would otherwise have entered. A similar pipette and manometer were connected with the air tube B. In order to be able, if desired, to follow with the eye a particular band during the changes of pressure (effected by small steps and alternately in the two tubes), diminutive windlasses were provided by which the motions of the reservoirs (E) could be made smooth and slow. In this way all doubt was obviated as to the identity of a band; but after a little experience the precaution was found to be unnecessary.

The manner of experimenting will now be evident. By adjustment of pressures the centre of the middle band was brought to a definite position, determined by the web or otherwise, and the pressures were measured. Both pressures were then altered and adjusted until the band was brought back precisely to its original position. The ratio of the changes of pressure is the inverse ratio of the refractivities $(\mu-1)$ of the gases. The process may be repeated backwards and forwards any number of times, so as to eliminate in great degree errors of the settings and of the pressure readings.

During these observations a curious effect was noticed, made possible by the independent action of the parts of the object-glass situated at various levels, as already referred to. When the bands were stationary, they appeared straight, or nearly so, but when in motion, owing to changes of pressure, they became curved, even in passing the fiducial position, and always in such a manner that the *ends* led. The explanation is readily seen to depend upon the temporary changes of temperature which accompany compression or rarefaction. The full effect of a compression, for example, would not be attained until the gas had cooled back to its normal temperature, and this recovery of temperature would occur more quickly at the top and bottom, where the gas is in proximity to the metal, than in the central part of the tube.

The success of the measures evidently requires that there should be no apparent movement of the bands apart from real retardations in the tubes. As the apparatus was at first arranged, this condition was insufficiently satisfied. Although all the parts were carried upon the walls of the room, frequent and somewhat sudden displacements of the bands relatively to the web were seen to occur, probably in consequence of the use of wood in some of the supports. The observations could easily be arranged in such a manner that no systematic error could thence enter, but the agreement of individual measures was impaired. Subsequently a remedy was found in the use of a second system of bands, formed by light which passed just above the

tubes, to which, instead of to the web, the movable bands were referred. The coincidence of the two systems could be observed with accuracy, and was found to be maintained in spite of movements of both relatively to the web.

In the comparisons of argon and air (with nearly the same refractivities) the changes of pressure employed were about 8 in. (20 cm.), being deductions from the atmospheric pressure. In one observation of July 26, the numbers, representing suctions in inches of mercury, stood

Argon.	Air.
8·54	9·96
0·01	1·77
8·53	8·19

Ratio = 0·961,

signifying that 8·53 in. of argon balanced 8·19 in. of dry air. Four sets, during which the air and argon (from the globe as last filled for weighing) were changed, taken on July 17, 18, 19, 26, gave respectively for the final ratio 0·962, 0·961, 0·961, 0·960, or as the mean

$$\frac{\text{Refractivity of argon}}{\text{Refractivity of air}} = 0{\cdot}961.$$

The evidence from the refractivities, as well as from the weights, is very unfavourable to the view that argon is an allotropic form of nitrogen such as would be denoted by N_3.

The above measurements, having been made with lamp-light, refer to the most luminous region of the spectrum, say in the neighbourhood of D. But since no change in the appearance of the bands at the two settings could be detected, the inference is that the dispersions of the two gases are approximately the same, so that the above ratio would not be much changed, even if another part of the spectrum were chosen. It may be remarked that the displacement actually compensated in the above experiments amounted to about forty bands, each band corresponding to about $\frac{1}{5}$ in. (5 mm.) pressure of mercury.

Similar comparisons have been made between air and helium. The latter gas, prepared by Professor Ramsay, was brought from London by Mr. W. Randall, who further gave valuable assistance in the manipulations. It appeared at once that the refractivity of helium was remarkably low, 13 in. pressure of the gas being balanced by less than 2 in. pressure of air. The ratios given by single comparisons on July 29 were 0·147, 0·146, 0·145, 0·146, mean 0·146; and on July 30 0·147, 0·147, 0·145, 0·145, mean 0·146. The observations were not made under ideal conditions, on account of the smallness of

the changes of air pressure; but we may conclude that with considerable approximation

$$\frac{\text{Refractivity of helium}}{\text{Refractivity of air}} = 0{\cdot}146.$$

The lowest refractivity previously known is that of hydrogen, nearly 0·5 of that of air.

Viscosity of Argon and Helium.

The viscosity was investigated by the method of passage through capillary tubes. The approximate formula has been investigated by O. Meyer,* on the basis of Stokes' theory for incompressible fluids. If the driving pressure $(p_1 - p_2)$ is not too great, the volume V_2 delivered in time t through a tube of radius R and length λ is given by

$$V_2 = \pi t \frac{p_1^2 - p_2^2}{2p_2} \frac{R^4}{8\eta\lambda},$$

the volume being measured at the lower pressure p_2, and η denoting the viscosity of the gas. In the comparison of different gases V_2, p_1, p_2, R, λ may be the same, and then η is proportioual to t.

In the apparatus employed two gas pipettes and manometers, somewhat similar to those shown in fig. 2, were connected by a capillary tube of very small bore and about 1 metre long. The volume V_2 was about 100 c.c., and was caused to pass by a pressure of a few centimetres of mercury, maintained as uniform as possible by means of the pipettes. There was a difficulty, almost inherent in the use of mercury, in securing the right pressures during the first few seconds of an experiment; but this was not of much importance as the whole time t amounted to several minutes. The apparatus was tested upon hydrogen, and was found to give the received numbers with sufficient accuracy. The results, referred to dry air, were for helium 0·96; and for argon 1·21, somewhat higher than for oxygen which at present stands at the head of the list of the principal gases.

Gas from the Bath Springs.

In the original memoir upon argon† results were given of weighings of the residue from the Bath gas after removal of oxygen, carbonic anhydride, and moisture, from which it appeared that the proportion of argon was only one-half of that contained in the residue, after similar treatment, from the atmosphere. After the discovery of helium by Professor Ramsay, the question presented

* 'Pogg. Ann.,' vol. 127, p. 270, 1866.

† Rayleigh and Ramsay, 'Phil. Trans.,' A, vol. 186, p. 227, 1895.

itself as to whether this conclusion might not be disturbed by the presence in the Bath gas of helium, whose lightness would tend to compensate the extra density of argon.

An examination of the gas which had stood in my laboratory more than a year having shown that it still contained no oxygen, it was thought worth while to remove the nitrogen so as to determine the proportion that would refuse oxidation. For this purpose 200 c.c. were worked up with oxygen until the volume, free from nitrogen, was reduced to 8 c.c. On treatment with pyrogallol and alkali the residue measured 3·3 c.c., representing argon, and helium, if present. On sparking the residue at atmospheric pressure and examining the spectrum, it was seen to be mainly that of argon, but with an unmistakable exhibition of D_3. At atmospheric pressure this line appears very diffuse in a spectroscope of rather high power, but the place was correct.

From another sample of residue from the Bath gas, vacuum tubes were charged by my son, Mr. R. J. Strutt, and some of them showed D_3 sharply defined and precisely coincident with the line of helium in a vacuum tube prepared by Professor Ramsay.

Although the presence of helium in the Bath gas is not doubtful, the quantity seems insufficient to explain the low density found in October, 1894. In order to reconcile that density with the proportion of residue ($3·3/200 = 0·016$) found in the experiment just described, it would be necessary to suppose that the helium amounted to 25 per cent. of the whole residue of argon and helium. Experiment, however, proved that a mixture of argon and helium containing 10 per cent. of the latter gas showed D_3 more plainly than did the Bath residue. It is just possible that some of the helium was lost by diffusion during the long interval between the experiments whose results are combined in the above estimate.

Buxton Gas.

Gas from the Buxton springs, kindly collected for me by Mr. A McDougall, was found to contain no appreciable oxygen. The argon amounted to about 2 per cent. of the volume. When its spectrum was examined, the presence of D_3 was suspected, but the appearance was too feeble to allow of a definite statement being made. The proportion of helium is in any case very much lower than in the Bath gas.

Is Helium Contained in the Atmosphere ?

Apart from its independent interest, this question is important in connection with the density of atmospheric argon. Since the spectrum of this gas does not show the line D_3, we may probably conclude

that the proportion of helium is less than 3 per cent.; so that there would be less than 3×10^{-4} of helium in the atmosphere. The experiment about to be described was an attempt to carry the matter further, and is founded upon the observation by Professor Ramsay, that the solubility of helium in water is only 0·007, less than one-fifth of that which we found for argon.*

It is evident that if a mixture of helium and argon be dissolved in water until there is only a small fraction remaining over, the proportion of helium will be much increased in the residue. Two experiments have been made, of which that on October 6, 1895, was the more elaborate. About 60 c.c. of argon were shaken for a long time with well boiled water contained in a large flask. When the absorption had ceased, the residue of 30 c.c. was sparked with a little oxygen until no nitrogen could be seen in the spectrum. It was then treated a second time with boiled water until its volume was reduced to $1\frac{1}{2}$ c.c. With this vacuum tubes were charged by my son at two different pressures. In none of them could D_3 be detected; nor was there any marked difference to be seen between the spectra of the washed and the unwashed argon. If helium be present in the atmosphere, it must be in very small quantity, probably much less than a ten-thousandth part.

Presents, January 16, 1896.

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* 'Phil. Trans.,' A, vol. 186, p. 225, 1895.

FIG. 2.