Argon and Its Companions

William Ramsay and Morris W. Travers

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II. *Argon and its Companions.*

By WILLIAM RAMSAY, *F.R.S., and* MORRIS W. TRAVERS.

[PLATES 1–3.]

"*Natura nihil agit frustra*, is the only indisputed Axiome in Philosophy. There are no Grotesques in Nature; not anything framed to fill up empty Cantons, and unnecessary spaces."—SIR THOMAS BROWNE'S 'Religio Medici.'

CONTENTS.

INTRODUCTION.

ON June 9, 1898, we had the honour of giving the Society a preliminary account of "Krypton, a new Constituent of Atmospheric Air"; and on June 16, we brought to the notice of the Society the existence of two other gases in air, which we named "Neon" and "Metargon." And at the meeting of the British Association at Bristol, we gave a further short account of these gases, and also announced the discovery of yet another gas, still heavier than the former, which we named "Xenon." In a note to 'Nature' in October, 1898, Mr. BALY called attention to the presence of helium lines in the spectrum of neon; the D_3 line had been previously remarked in atmospheric air by Professor KAYSER, of Bonn ('Chemical News,' August 23, 1895), and by Dr. FRIEDLÄNDER, of Berlin (*ibid.*, December 9, 1895).

Since publishing the preliminary notes referred to, we have been engaged in a study of these gases; and we may say at the outset that we have failed to isolate

29.7.1901.

" Metargon." It will be remembered that Professor SCHUSTER, in a letter to 'Nature' (vol. 58, p, 199, June 30, 1898) pointed out that the spectrum of metargon presents a close analogy with that of carbon in the "Swan" spectrum. This we verified, and subjected the gas to prolonged sparking with oxygen in presence of caustic soda, attempting thus to oxidise and remove the carbon compound. The carbon spectrum was, however, still visible in a "Plücker" tube at a pressure of several millimetres of mercury. We were inclined to ascribe this spectrum to the presence of a compound of carbon with one of the usually inert gases. But we have since failed to detect this spectrum ; and we think it probable that in removing oxygen from the sparked gas some carbon was introduced with the phosphorus we then used. REMSEN (' American Chemical Journal,' V, No. 6) has drawn attention to the fact that some specimens of yellow phosphorus contain carbon, probably in combination, and that on burning the phosphorus, carbon monoxide and dioxide are formed. After the supposed purification from carbon compounds, we must have introduced carbon monoxide into the argon of which the bulk of the sample of gas consisted, and still recognising a spectrum similar to that of carbon, we ascribed it to the presence of " metargon." The phosphorus we at present employ does not produce such a spectrum, and we must therefore withdraw our statements regarding this supposed gas.

On making a mixture of pure yellow phosphorus with powdered charcoal, and using it to remove oxygen from argon, the spectrum of the remaining gas was identical with that which we described as " metargon," even to the bright bands in the violet, which are not present in the spectrum of pure carbon monoxide, but which are visible in that of cyanogen. Some crude phosphorus, kindly given us by Mr. GEORGE ALBRIGHT, gave the same spectrum, when used to remove oxygen from argon.

We can only express our regret that such a simple cause has led us into an erroneous statement, which we here retract.

It will be seen from what follows that the inert gases of the atmosphere form a well-defined series parallel to that of the halogens, and of the metals of the alkalies. Thus we have :—

?	Fluorine.	Chlorine.	Bromine.	Iodine.
Helium.	Neon.	Argon.	Krypton.	Xenon.
Lithium.	Sodium.	Potassium.	Rubidium.	Cæsium.

It is unlikely that any gas possessing an atomic weight higher than that of xenon is to be found in atmospheric air. The question as to the precursor of helium will be discussed later. The atomic weights of these gases are taken as twice their densities, on the apparently well-founded assumption that the ratio 1·66 between the specific heat at constant volume and that at constant pressure implies that the molecule and the atom are identical. If this assumption, which is fully justified on physical grounds, is denied, then these elements can find no place in the periodic

table. This conclusion, as will be shown when the question of their atomic weights is discussed, is wholly untenable.

The separation of these gases from air, and from one another, is a very troublesome one, and demands much time and patience. Moreover, the tests of purity are not easily applied. The pocket spectroscope is, of course, a useful instrument, when it is required to decide as to the nature of the main constituent of a gaseous mixture. It is convenient, in using the instrument, to remove the lenses and the slit, and to examine the capillary portion of the Plücker tube at a distance of 6 or 8 feet. The brightly illuminated capillary then itself forms a sufficiently good slit, and the spectrum is a very luminous one. This plan, however, fails when one gas is contaminated by traces of others. By altering the pressure in the Plücker tube, and by interposing a jar and a spark-gap, it is often possible to reveal the presence of a small proportion of one of these gases in a large amount of another. But at the best it is only a rough guide. The final criterion of purity was always the balance. If two portions of gas were found to possess nearly the same density, they were fractionated and their density again compared. If the density was not altered by fractionation, they were regarded as homogeneous and identical.

Apparatus employed in these Researches.

It will conduce to brevity and clearness, if we begin with an account of the apparatus and methods which we found advantageous in preparing the liquid air, in fractionating the gases, in determining their density, their refractivity, their molecular volumes, their compressibilities, and in measuring their vapour-pressures. In some cases, the methods have been employed before, and where this has been the case, we will confine our description to any modifications which we have found useful for the particular purpose in view, giving references to the papers previously published on the subject.

*The Liquefaction of Air** was carried out by means of an apparatus built from the design of the inventor, Dr. HAMPSON, by the "Brin" Oxygen Company. Its principle, which is common to Dr. LINDE's machine, consists in the expansion of air compressed under a pressure of 150 to 175 atmospheres, through a valve L regulated by the spindle M; the "Thomson-Joule" effect is thus utilised, and the expanded air passes upwards over the surface of the coils KK, through which it has passed downwards in a state of compression, thereby cooling the coils progressively, and absorbing more and more heat in expanding, until the temperature is ultimately reduced to below the temperature at which the air liquefies. The liquid collects in the vacuum-vessel N and can be drawn off at the stop-cock O. The

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* Up till April, 1899, we obtained our supplies of liquid air from Brin's Oxygen Company, and we take this opportunity of expressing our sincere thanks to Mr. MURRAY and Dr. HAMPSON for their kindness in furnishing it.
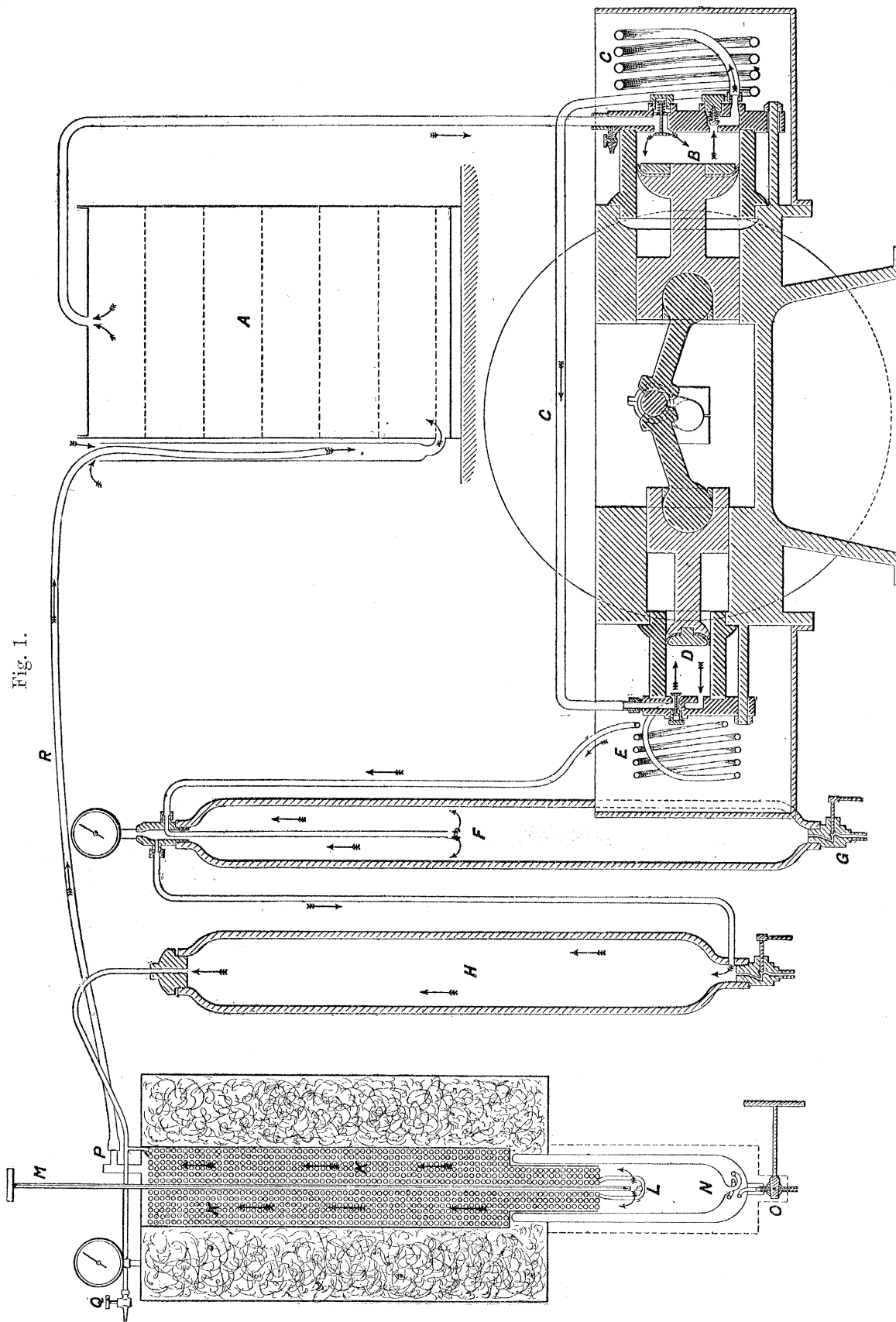
Fig. 1.

air is compressed by a "torpedo air-compressor" made by the Whitehead Company of Fiume, Austria; it enters the compressor through a low-pressure purifier A, consisting of a drum fitted with trays, each covered with slaked lime, to effect a preliminary absorption of carbon dioxide. In the first cylinder, B, it is compressed with a pressure of about 60 atmospheres, and passes through a tube C to the intake valve of the second cylinder D, where the pressure is raised as high as is desirable; the air then passes through the cooling coil E to the separator F, where the water which enters the cylinders for the purpose of lubrication, is separated and discharged at the cock G; it passes through a high-pressure purifier H, charged with caustic potash in lumps, which removes water-vapour, and any carbon dioxide which may have escaped absorption in the low-pressure purifier. From the high-pressure purifier, it enters the liquefier. The power required to drive the compressor is about five horse-power; and when working at a pressure of 175 atmospheres, it delivers a litre-and-a-quarter of liquid air per hour. The air begins to run liquid in eight minutes after starting the compressor; and the amount of attention it requires is no more than that of an ordinary steam-engine, in oiling, cleaning, &c.

The apparatus employed in fractionating the gases was similar to that described in the 'Proceedings,' vol. 64, p. 188. To that description there is nothing to add, save that the bulb b in the figure is relatively much smaller, when only small amounts of gas are available; and the tube-reservoir a, had a capacity of 35 cub. centims. It was also possible to compress the gas in a by raising the attached reservoir,

Fig. 2.

H 2
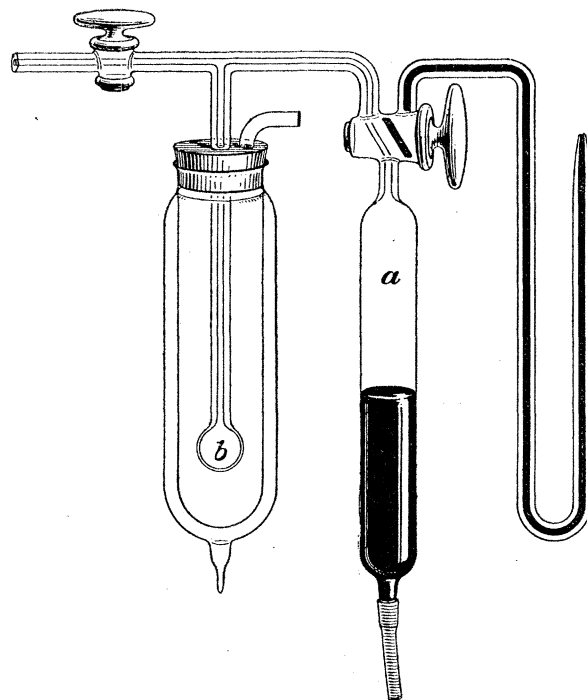
under a pressure of over an additional atmosphere, in order to facilitate liquefaction. This device was particularly useful in the separation of neon from argon, and in the liquefaction of argon, mixed with the heavier gases, which could then be accomplished without the necessity of causing the air to boil at reduced pressure.

By enclosing the vacuum-vessel shown in the diagram in a wider outer vessel, filled with liquid air, and by reducing pressure in the inner vessel, the temperature could be reduced as low as 205° and maintained with hardly any labour, owing to the very slow ingress of heat. This device was particularly useful in the separation of neon from argon; but it was unnecessary in the separation of argon from the heavier gases.

Determination of Density.—As the densities of the gases obtained by the process of fractional distillation gave us the surest indication of the manner in which the fractionation was progressing, very many determinations were made during the course of the investigation. Except in the case of argon itself, the quantities of gas at our disposal were exceedingly small; and we were consequently obliged to reduce the dimensions of the weighing globes to the smallest capacity compatible with the degree of accuracy which we desired to attain, and to design a combined gasholder and manometer for introducing as much of the gas as possible into the globe.

Some four years ago, in conjunction with Dr. NORMAN COLLIE, in a paper read before the Chemical Society, we pointed to the possibility of determining the density of helium to within 1 per cent. above or below its actual value by weighing the gas in a globe of about 30 cub. centims. capacity. The results obtained for the much heavier gas, argon, naturally showed much closer concordance; and we have found that the accuracy of such experiments is conditioned only by the sensibility of the balance. Since neon, the lightest of the new gases, is five times as heavy as helium, we resolved to employ a globe of 7 cub. centims. capacity. Determinations of the density of the same sample of gas, carried out by each of us independently, showed that it was possible to obtain results of sufficient accuracy and concordance, even when the pressure on the gas did not exceed 250 millims. of mercury; this statement is substantiated by the figures in the following table :—

The gas chosen is neon containing helium; the capacity of the bulb is 7·152 cub. centims.

	Weight of gas.	Pressure.	Temperature.	Density.
	grammes.	millims.	°	
W. R.	0·00531	788·6	16·20	8·48
M. W. T.	0·00339	507·1	16·95	8·44
W. R.	0·00331	422·5	18·40	9·94
M. W. T.	0·00320	417·2	20·15	9·80

In these and all other determinations, the density has been referred to $O = 16$.

The Weighing Globes.—Three globes were employed of capacities corresponding to

163·170 cub. centims., 32·138 cub. centims., and 7·152 cub. centims. ; the largest was used only to determine the density of pure argon. Sealed glass globes of the same external volume as the weighing globes were used as counterpoises.

The Weights.—The values of the weights were carefully referred to that of a centigramme rider. It was not necessary to know their absolute values, for since the volumes of the globes were obtained by weighing them filled with water at a known temperature with the same weights as were used in weighing the gases, the weights of the gases were referred through the weight of an equal volume of water to the weight of an equal volume of oxygen. The weight of a litre of oxygen was taken as 1·4296 gram. (' Phil. Trans.,' A, 1895, Part 1, p. 201)*.

The Balance.—The globes were weighed in a long-beam Oertling balance to 0·01 milligram. They were usually allowed to hang for about half-an-hour in the balance-case, before the final weighing was made.

The Preparation of the Gases.—The gases were sparked with oxygen in presence of caustic soda to remove nitrogen, &c. ; the oxygen was subsequently removed by means of phosphorus, the water-vapour being at the same time absorbed by the products of its combustion. As this process differs somewhat from any previously described, it may be advisable to enter into it in some detail. After the gas had been sparked, it was withdrawn into a burette, and separated from the soda. A tube was then completely filled with mercury, and a piece of phosphorus, as large as a small pea. was introduced, so that it floated up above the mercury. The top of the tube was then warmed, so as to melt the phosphorus, and the gas was introduced from the gas-burette, through the mercury, bubble by bubble ; as each bubble entered it caused the phosphorus to inflame. When all the gas had been introduced, the top of the tube was again warmed, and a rain of phosphorus fell through the tube. After cooling, the gas could be withdrawn if desired ; but it was often kept in the same tube until required. It appears to be necessary to have a sufficiency of oxygen in the gas which is admitted to the phosphorus ; for if the phosphorus does not inflame, we have found that the spectrum shows lines belonging to phosphorus ; if, however, the phosphorus actually catches fire, there is no sign of any volatile compound being present in the gas.

The apparatus employed for introducing the gas into the globe is shown in fig. 3. The gas can be introduced through the siphon into the burette A, which can be placed in communication with the globe E. The side-tube B, which is of the same diameter as the upper part of the burette, facilitates the measurement of the pressure on the gas, after it has been allowed to fill the globe, thus eliminating any correction for capillarity. The pressure was read off on a silvered glass scale, to which the burette was fixed. The tube *c*, which was about 2·5 millims. in diameter, contained a roll of

* In previous determinations with the same bulbs different weights were used, and the capacity is given as a slightly different number. As these were also referred to water, no correction as regards the densities previously determined is necessary.

amalgamated silver-foil, which effectually retained any small globule of mercury which might have been carried over into the globe E by the stream of gas. The apparatus communicated with the pump through the stop-cock c.

Fig. 3.
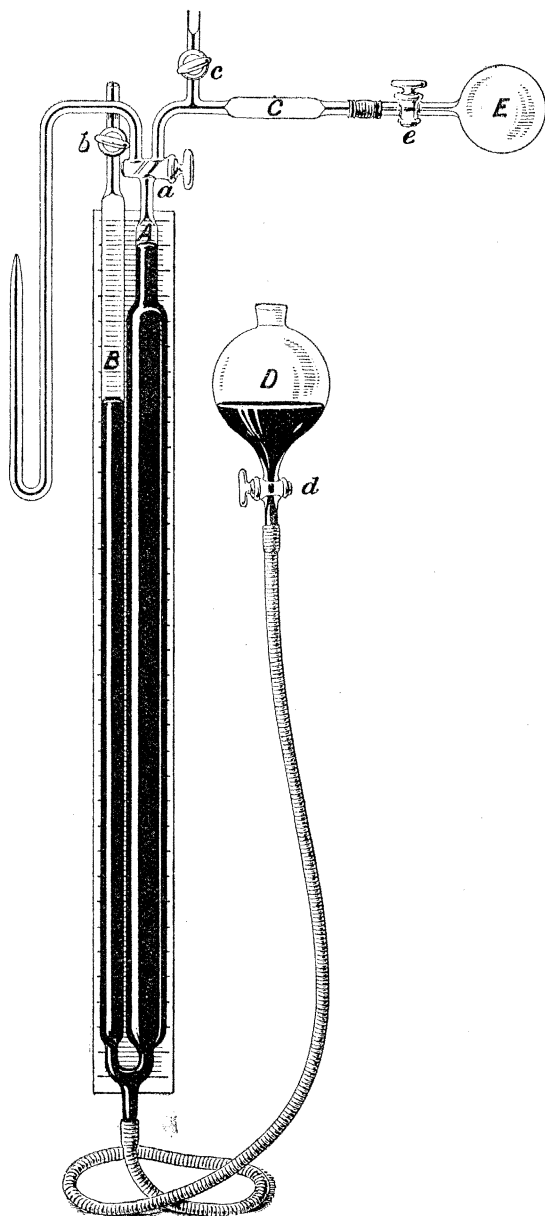
The method of manipulation was briefly as follows. The apparatus was first filled with mercury to the level of the stop-cocks a and b, which were closed ; the reservoir D was then lowered, so as to leave a barometric vacuum in the tubes A and B; the stop-cock d was then closed. The globe E was now attached to C by a short length of thick-walled india-rubber tubing, which was wired at both ends ; the globe itself was enclosed in a small cardboard box, which also contained the bulb of the thermometer. The stop-cocks a, c, and e were now turned, so as to place the whole of the apparatus in communication with the pump. It was particularly important to remove the air in the bore of the stop-cock a, as its volume was not inconsiderable in comparison with that of the gas weighed. After exhausting the apparatus, the stop-cock a was closed, and by turning the stop-cock d, the mercury was allowed to rise in the burette. The gas was then introduced through the siphon into the burette, and the stop-cock c was closed. On turning the stop-cock a, the gas entered the globe, while the reservoir D was held in such a position that the mercury did not rise above a. The stop-cock b was then opened, the stop-cock a being momentarily closed, in order to avoid any danger of mercury being forced up into C ; and the position of the reservoir D was adjusted, so that the surface of the mercury in A lay as near as possible to the top of the tube. After about a quarter of an hour, the temperature and pressure were observed, the stop-cock e was closed, and the barometer was read. The gas contained in the tube C and in the burette was removed by exhaustion, and collected through the pump, and the globe was detached from the apparatus and suspended in the balance.

After weighing the globe, it was again attached to the apparatus, and when the tube C had been exhausted, the stop-cock e was opened, and the gas was removed from the globe through the pump. The globe was then weighed empty, and from the difference of the two weighings the weight of the gas was determined. With a globe of the small size of those employed it was unnecessary to apply any correction for shrinkage under atmospheric pressure.

The Preparation of Neon.

The process which led to the discovery of neon was the fractionation of a large quantity of liquid argon. A partial description of this has already been given in the ' Proceedings,' vol. 64, p. 188, where we have described the preparation and some of the properties of pure argon; and also in a note " On the Companions of Argon," vol. 63, p. 437. But for the sake of completeness, we shall briefly recapitulate the main points.

The whole of the argon which we had made, probably about 15 litres, was liquefied in a bulb immersed in liquid air boiling under reduced pressure. The bulb was then placed in communication with a series of mercury reservoirs, and successive fractions of gas were collected; the remaining liquid was then allowed to evaporate, and the gas was returned to the gasometer in which it had originally been stored. The first fraction of gas turned out to be rich in neon, and was afterwards found to contain helium. After repeated fractionation its density was reduced to 14.

The main quantity of the argon was submitted to a second fractionation, and a further quantity of neon was obtained. A third liquefaction of the argon yielded a first distillate, of which the density was only slightly lower than that of argon, viz., 19·05. After one-sixth of the argon had evaporated, the remaining fractions manifested no further change in density; and it was therefore assumed that the middle fractions consisted of pure argon.

The gas of density 14 was refractionated by means of the apparatus shown in fig. 2. The gas was introduced from the gasholder a into the bulb b, which was immersed in liquid air, boiling under reduced pressure. The apparatus communicated with a Töpler pump through the stop-cock; before admitting the gas, all air had been removed. On raising the reservoir attached to a, and applying an additional atmosphere's pressure, the mixture of neon and argon condensed in the bulb b. The stop-cock on the gasholder a was then closed, and the liquid was allowed to stand for a few minutes, so that it might become homogeneous.

On lowering the mercury reservoir, and opening the stop-cock, a portion of the gas, about one-fifth of the whole, was allowed to boil off into the gasholder, the temperature of the bulb being kept as low as possible. This fraction of the gas, which contained the greater quantity of the lower-boiling constituents, was transferred to a tube, and a second, third, and fourth fraction were taken off in the same manner. The last fraction was removed through the pump, and collected as usual. These five fractions, consisting of approximately equal quantities of gas, formed

a series of ascending densities; they are represented by the numbers 2 to 6 in the annexed table. The method employed for their further fractionation was as follows :—

TABLE I.

```
                                                   ┌16┐
                                        ┌13┐       │17├─22─        ┌28─
                                        │   │      └18┤   ┌─       │   ┐─30─  ─Neon and helium.
              ┌2 (13·4)┐   ┌7 (9·7)─    │14─┤   ┌─19┘  23 (8·3)   └29┘
              │3 (16·2)│   │8  —        └15 ┤   │                      31 (8·3)─┐ ┌34 (8·3)
   1 (14·0)   │4 (16·6)│   │9 (16·5)       └──20┘                      32─────  └35 (9·8)
              │5 (17·2)│   │10 —                                       33─
              └6  —    ┘   │11 (17·7)      ┌21─24   (10·6)
                          └12 —                 25──────────        Neon and argon.
                                                26──────────
                                             └27──────────
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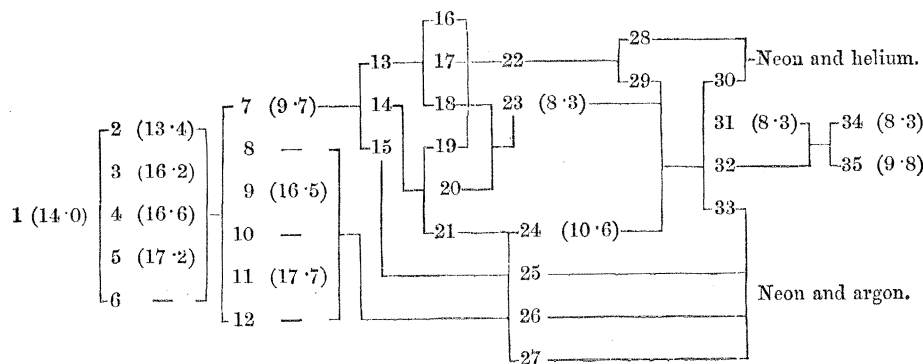
The heaviest portion 6 was placed in the gasholder, and liquefied in the bulb; a portion of it was allowed to boil off into the gasholder; and the remainder (the heavier portion 12) was transferred to a tube. The next heaviest portion 5 was then placed in the gasholder, liquefied together with the gas already in the bulb, and subsequently divided by evaporation into two portions. This operation was repeated in the case of each fraction, the proportion of gas taken back into the gasholder increasing at each operation so as to produce six approximately equal fractions, represented in the table by numbers 7 to 12.

This process, as is clearly shown in the table, resulted in the separation of the heavy and light constituents of the mixture with a certain degree of sharpness. Fraction 7, when examined spectroscopically, was found to contain only a trace of argon, while fraction 12 consisted almost entirely of that gas; beyond this, it was found that the gas of density 9·7 could not be liquefied at —200° under a pressure of two atmospheres.

In order to determine whether fraction 7 consisted of homogeneous gas, mixed with only a trace of argon, it was necessary to fractionate it further, and to submit each fraction to a rigid spectroscopic examination. Since the gas would not liquefy, it was mixed with about eight times its volume of oxygen; the mixture was liquefied in the apparatus, and the liquid was allowed to evaporate in three fractions, Nos. 13, 14, and 15. After the oxygen had been removed from the inactive residue, it was found that in the third fraction (15) alone, could argon be detected by visual observation of the spectrum. When, however, the spectrum of the lighter fraction was photographed, it was found that the lines represented by the wave-lengths 5876 and 5016 were present. The gas contained helium, which is accordingly present in the atmosphere; KAYSER's and FRIEDLÄNDER's observations were confirmed. After knowing that they were present, it was possible to see the principal helium lines with a direct-vision spectroscope.

This observation introduced a new feature into the work; for, although no great difficulty had been experienced in the separation of the light gas from argon, it appeared likely that the separation of two gases so nearly akin as helium and neon would be considerably more troublesome. And this proved to be the case.

The next stage in the fractionation consisted in the separation of fractions 13 and 14 each into three parts by mixing them with oxygen, and distilling the mixture. The oxygen was removed from each fraction separately; and after spectroscopic examination, the fractions 16, 17, and 19, which contained the greatest quantity of helium, were mixed, as were also fractions 18 and 20, which consisted of nearly pure neon. The density of the latter, 23, was 8·3. The fractions 8 to 12, with 15 and 21, were also submitted to a further fractionation yielding about 20 cub. centims. of neon of density 10·6, containing only a little argon.

Up to this point, the gas had been divided into five portions :—

    i. (22), consisting of neon with much helium ;
    ii. (23)   ,,   ,,   trace of helium ; (D = 8·3)
    iii. (24)   ,,   ,,   trace of argon ; (D = 10·6)
    iv. (25)   ,,   ,,   much argon ;
    v. (26) and (27) residues.

Following this scheme, fraction 22 was divided into two parts, and the fraction containing least helium (29) was mixed with fractions 23 and 24. This gas, mixed with oxygen, was liquefied and divided into four parts, the lightest containing helium, and the heaviest, argon. The two middle fractions, 31 and 32, were mixed, and after addition of excess of oxygen, were again fractionated. The lightest fraction, amounting to about 10 cub. centims., had a density of 8·3, and still contained helium ; fraction 35, amounting to 5 cub. centims., had the density 9·8 ; and a third fraction not numbered, for it consisted only of a single small bubble of gas, showed distinctly the spectrum of argon. We regarded the sample of density 9·8 as the purest ; but there is no doubt that it still contained both helium and argon.

It appeared, therefore, an almost impossible task to separate these gases by fractionation. If it had been possible to liquefy the mixture without addition of oxygen, separation might have been thus accomplished ; but fractionation under these circumstances can only be only an incomplete operation ; and we therefore resolved to attempt another plan. But for this, a larger quantity of neon was required, and a method of separation from the oxygen and nitrogen of the air, which we shall now describe, was devised.

In describing the compressor (fig. 1), it was mentioned that the air drawn in had passed through a low-pressure purifier, filled with trays charged with slaked lime, in order to remove carbon dioxide. As a rule, the air which had escaped liquefaction was allowed to blow off through the nozzle Q and mix with the atmosphere. But by causing it to blow through an india-rubber tube R, the further end of which

delivered into the intake of the low-pressure purifier A, the same air was returned into the compressor; the amount which had been liquefied was replaced by ordinary air, drawn into the purifier, and from it to the compressor, at the same time. In this manner the air which passed through the liquefier was fractionated and refractionated, for the heavier and more condensable portions were continually removed, while the lighter portions passed again through the machine. The escape valve, Q, at the top of the liquefier (fig. 1) was connected by thick-walled india-rubber tubing with the bulb a (fig. 4) immersed in a vacuum-jacket which was filled with the liquid air continually being produced during the process; that is, with the portion which had condensed from the total quantity entering the machine. The boiling point of this liquid air was unusually low, for it contained, owing to the process of circulation, a larger proportion of nitrogen than usual. The air entering the bulb a was under an additional pressure of about an atmosphere and a half, as shown by a gauge. When the bulb a was filled with liquid to near the top, the

Fig. 4.
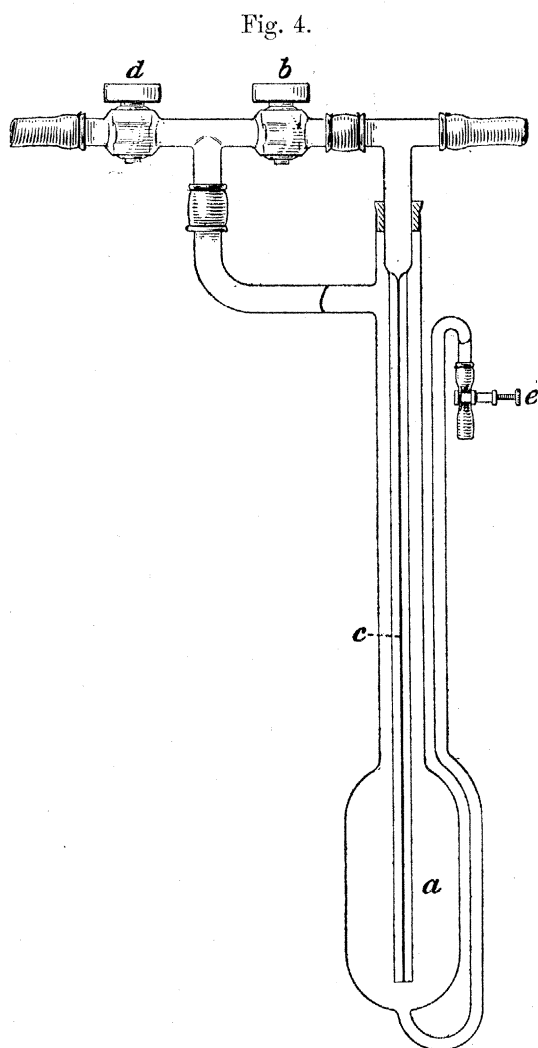
stop-cock b was shut, so that the compressed air no longer freely entered the bulb, but passed through the narrow tube c, and bubbled through the liquid in the bulb. On opening the stop-cock d, which communicated with a tube leading to a large gasholder, the liquid in the bulb evaporated; when about one-sixth had boiled off into the gasholder, this part of the operation was stopped; and by shutting the stop-cocks b and d, and opening the clip e, the liquid in the bulb was forced out, and flowed into the outside jacket, increasing the volume of air employed for the purpose of condensation. In this manner, the gasholder, of about 120 litres capacity, was filled with the lightest and lowest-boiling portion of liquid air. In case others may desire to repeat this operation, a word of caution may be given: it is absolutely necessary to blow air through the contents of the liquefying bulb, while evaporation is proceeding; if this is not done, evaporation takes place chiefly from the surface, and the gas collected in the gasholder will contain very little neon; it was only after several unsuccessful trials that we dis-

covered the cause of our failure to obtain gas rich in neon. Moreover, liquid nitrogen is very apt to become superheated, and to boil from the surface.*

The gas contained in the gasholder was freed from oxygen, of which there was very little present, by burning with hydrogen, as described later; and from nitrogen, of which it chiefly consists, by a red-hot mixture of lime and magnesium. From about 120 litres of the light air, about 800 cub. centims. of argon comparatively rich in neon was obtained; it was fractionated, in a manner similar to that described on p. 55, mixing it with nitrogen instead of oxygen; for it was supposed that neon might have a somewhat greater solubility in the lower-boiling liquid. No improvement was noticed; hence the further fractional solution was carried out with oxygen as a solvent, the temperature being lowered to −205°, by causing the oxygen to boil under reduced pressure (see p. 52). The gas obtained by the last process, together with the lighter fractions from previous operations (34 and 35), were condensed with 200 cub. centims. of oxygen, and the liquid was evaporated in six fractions (36 to 41); of these, the last three (39, 40, and 41) were discarded, as consisting mainly of argon; the gas was examined spectroscopically after removal of the oxygen with phosphorus. The first three portions were divided into five (42 to 46), and the last fraction was again discarded after examination. In each case, the last fraction consisted of the main bulk of the oxygen. The operation was repeated with the first three fractions (42, 43, and 44), giving four portions (47 to 50); the last fraction was mixed with No. 45. These fractions contained argon, and it was hoped that they would contain but little helium.

The operations described are shown diagrammatically on the table which follows:—
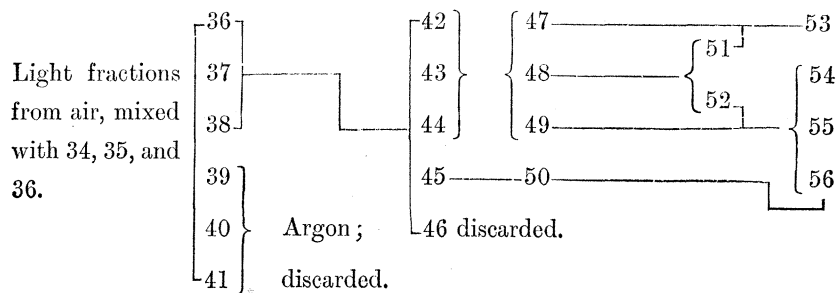
It was supposed that Nos. 53, 54, and 55 contained helium and no argon, and that 56 contained no helium, but a fair amount of argon. The first three of these were again fractionated, and a small quantity of argon was found in the oxygen remaining after the chief part of the gas had evaporated; this operation was repeated, and a trace of argon was again discarded, thus:—

* We owe our thanks to Messrs. GRAY HEHNER and LIDBURY for kindly superintending this operation.

$$
\begin{array}{ll}
 & \text{Density.} \\
53\,\Big\} & 57\,\Big\} \quad 61\ .\ .\ .\ .\ 7\cdot24 \\
54\,\Big\}-\Big\{\ 58\,\Big\}-\Big\{\ 62\ .\ .\ .\ .\ 7\cdot52 \\
55\,\Big\} & 59\,\Big\} \quad 63\ .\ .\ .\ .\ 8\cdot27 \\
 & 60\!-\!\!\wedge\!-\text{Argon; discarded.}\quad 64 \\
56\ .\ .\ .\ .\ .\ .\ .\ .\ .\ .\ 8\cdot57
\end{array}
$$

The density of 63 was not greatly different from that of 56, which contained argon, hence 63 also obviously contains that gas; these two were accordingly mixed, and liquefied along with 500 cub. centims. of oxygen; the mixture was collected in two portions, 65 and 66; the first fraction, 65, had the density 7·24; the last, 66, contained nearly all the argon in these later samples.

It became a question whether it was possible to separate helium from neon by this process. It was obviously possible to remove practically all the argon; and this is not surprising, since the boiling-points of argon and oxygen are nearly the same; but an experiment to determine the relative solubilities of helium and of the impure neon which we possessed showed that there was no very great difference in favour of the latter. The solubility in oxygen at −205° of both gases was approximately 80 volumes of gas in 100 of liquid oxygen under normal pressure. The presence of argon greatly increases the solubility, and, indeed, these gases appear to be freely soluble in liquid argon. The results obtained by fractional solution in liquid oxygen were not sufficiently promising to induce us to continue the process.

The next attempt to free the neon from helium was made by means of diffusion. The density of helium being in round numbers 2, and that of neon presumably 10, the rate of diffusion of helium should be about twice as great as that of neon. A small diffusion apparatus similar to the one described in the 'Proceedings' (vol. 62, p. 318, A in figure) was employed, and a preliminary experiment with oxygen and hydrogen showed that it was possible to reduce the quantity of hydrogen considerably in one operation. Collecting the diffusate in three fractions of relative volumes, 59, 45, and 16 per cent. of the original, the last fraction contained only 16·5 per cent. of hydrogen; the percentage of hydrogen in the original mixture had been 54.

All the available neon, therefore, which had been freed from argon by fractional solution in liquid oxygen, was united; the density of the mixed samples was 7·3. It was divided by diffusion into three equal amounts, 1, 2, and 3, and these were further fractionated in the same manner as in conducting a fractional distillation; that is, fraction 1 was introduced into the diffusion apparatus, and the first portion which passed over was collected separately; portion 2 was then introduced, and the first portion of the diffusate was added to 1; the main bulk was collected in 2; and fraction 3 was added to the gas remaining in the diffusion apparatus, the first portion of the diffusate being collected in tube 2, and the remainder in tube 3. This

operation was repeated three times; the lightest portion showed the helium spectrum with brilliancy. During the third fractionation, the diffusate was collected in four fractions. The density of the heaviest was 8·90, and of the lightest, 6·24. The heaviest fraction was again diffused, and the first quarter was rejected; the density of the remainder had risen to 9·18. In each case the gas was sparked with oxygen before it was weighed, so as to remove any accidental contamination. It was thus evident that 9·18 was a minimum density for neon.

As it was evident that no complete separation of neon from helium could be effected by means of any process of diffusion or solution, these attempts were given up. The separation was finally accomplished by means of liquid hydrogen, the operation being conducted in precisely the same manner as the separation of argon from krypton and xenon, and the latter two gases from each other by condensing them with liquid air.

The liquid hydrogen was made in an apparatus constructed by one of us (M. W. T.) with the valuable assistance of the laboratory mechanician, Mr. J. HOLDING. As it is described in detail elsewhere,* suffice it to say that hydrogen, made from zinc and sulphuric acid, and submitted to no further purification than by a rapid passage through a wash-bottle charged with a solution of potassium permanganate, was compressed by the Whitehead compressor into a set of coils cooled by liquid air boiling under low pressure; the hydrogen was allowed to expand through a jet to atmospheric pressure, at the end of a regenerator-coil, similar to that in the HAMPSON'S apparatus. The operation presents no special difficulty to those used to the Hampson liquefier, and the yield is rapid and ample. Any impurities can be easily separated by filtration. For complete separation of neon and helium, 100 cub. centims. is sufficient; for liquid hydrogen is fairly permanent, and does not evaporate much more quickly than liquid air.

On admitting the mixed gases into a bulb cooled by liquid hydrogen, all the gas at once entered, even under reduced pressure, there being sufficient neon present to dissolve and liquefy the helium. The pressure in the mercury gasholder was made very low, by depressing the reservoir, and the first fraction of gas re-entered the gasholder. It consisted of helium, mixed with a trace of neon. It was set aside as not further needed. The residue was removed through the pump, and re-liquefied. The stop-cock to the pump being opened, a few bubbles were removed. The second fraction, which had a vapour-pressure of only a few millimetres at the boiling-point of liquid hydrogen, was removed by pumping; the residue, amounting to a few bubbles only, being kept separate, for it might possibly have contained a little argon, the vapour-pressure of which was practically zero at that temperature. It was pumped off after the removal of the liquid hydrogen. It is evident from the very low vapour-pressure of neon at the boiling-point of hydrogen that helium must have been completely removed by this process. It is true that a little neon was lost by

* 'Phil. Mag.,' 1901, vol. 1, p. 411.

neglecting to refractionate the first distillate : but as our object was to procure pure neon, and not pure helium, this was of no consequence.

The density of this neon was determined independently by each of us.

	W. R.	M. W. T.
Volume of bulb	32·038 cub. centims.	32·038 cub. centims.
Weight of gas	0·01100 gramme.	0·01120 gramme.
Pressure	306·5 millims.	313·8 millims.
Temperature	292·05° abs.	292·2° abs.
Density of neon	9·99	9·94

The Preparation of Krypton and Xenon.

These gases are left behind after the evaporation of liquid air, along with a large quantity of oxygen and some nitrogen. It has been necessary to use considerable quantities of liquid air for refrigerating purposes, and in almost all cases, the residue of a few cub. centims., instead of being allowed to evaporate away, was collected in a gasholder. When a sufficient quantity had accumulated, the oxygen was removed by combustion with hydrogen in the following manner :—

An iron tube, about half an inch in internal diameter, filled with platinised asbestos, was heated to redness in a long-flame gas burner. At one end of the tube an arrangement like a blowpipe was attached by screwing, and through one of the tubes a current of hydrogen entered from a KIPP's apparatus, while through the other the mixture containing the rare gases was admitted. These gases burned, and by regulating the stop-cocks, it was possible to adjust the proportions fairly well. But to make it possible to leave the operation to itself, and to render it in a sense automatic, a tell-tale tube of hard glass, containing copper oxide in one half, and metallic copper in the other, was connected with the other end of the iron tube : so that if excess of oxygen passed it oxidised the copper, and if excess of hydrogen, it reduced the copper oxide. The further end of the glass tube was connected with a reservoir, and with a gasholder. The water produced condensed in the reservoir, which was so arranged that it could be run off from time to time ; and the gases, now free from oxygen, passed into the gasholder. The nitrogen was next removed with a mixture of lime and magnesium. This mixture, as already stated by MAQUENNE, absorbs nitrogen at a much lower temperature than magnesium itself, and consequently it is not difficult to manipulate it in hard-glass tubes. The only precaution required is that the lime must be free from hydroxide and carbonate, for, if not, the magnesium is apt to act so quickly on these impurities as to produce a rush of gas,—hydrogen and carbon monoxide—so rapid as practically to amount to an explosion. The lime, therefore, should be made directly before use, by heating precipitated carbonate in a muffle for several hours ; and it is conveniently mixed with magnesium powder immediately before using, in about equal proportions. Care must be taken to pass the current of

gas containing nitrogen slowly over this mixture, heated to dull redness, else the temperature may rise so high as to cause the tube to fuse. There is no limit to the rapidity of the absorption, which is conditioned merely by the melting-point of the glass, for great heat is liberated by the reaction. The nitrogen is completely removed by this method, no trace being left behind; but as it is impossible to exclude all traces of carbonate or hydroxide, the gas collected always contains some hydrogen and carbon monoxide. These must be subsequently removed by passing the gas over copper oxide at a red heat, and absorbing in soda-lime the carbon dioxide produced.

The first preparation of krypton was described in the 'Proceedings,' vol. 63, p. 405; the density of the sample of argon showing the spectrum of krypton brilliantly was 22·5. But we were surprised to find that on refractionating, the density of the gas, instead of rising, fell. This we found subsequently due to the fact that the gas was pumped out of the fractionating bulb without removing the jacket of liquid air; and under these circumstances, the xenon, of which the density is 64, remained in the bulb. On one occasion, the jacket was removed; and the small remaining quantity was collected separately; it turned out to possess a spectrum totally differing from that of krypton, and was subsequently named "xenon." The spectrum of krypton is one which is remarkable for its brilliancy, and for the fact that a small amount of gas, present along with argon, is easily recognised by the spectroscope; and this led us to believe that krypton possessed a density not differing greatly from that of argon. Repeated fractionation, moreover, did not appear to produce any marked change in its character or brilliancy.

It would be tedious to relate in detail all the unsuccessful experiments which were made before the truth was discovered, that krypton is a gas present in very small quantity, but possessing a density of 40·8. Suffice it to state that the gas was fractionated more than twelve times, and that 24 determinations of density were made. We will, therefore, at once proceed to describe the method by which krypton and xenon were prepared in a pure state.

The gas remaining after the evaporation of the air used in various experiments, which we estimate as having been not less than 30 litres in all, was purified in the manner already described from oxygen and nitrogen. The remaining gas, of which, of course, argon constituted the main part, was liquefied and fractionated, so as to separate the heavier portion. The process employed in fractionation was as follows :—The heavy gas was liquefied in the apparatus described on page 51, at the temperature of liquid air. When it was rich in argon, some external pressure was necessary for liquefaction; but later, the gases liquefied, and when nearly pure, solidified, even under reduced pressure. The lighter portion was allowed to boil back into the gas-holder, and the remainder collected in one portion; this operation was repeated, and the remaining gas is alluded to as fraction 1.

The whole of this fraction, amounting to about 300 cub. centims., was introduced into the gasholder of the liquefaction apparatus, and was condensed at the

temperature of liquid air by applying a slight pressure. The liquid was then allowed to evaporate back into the gasholder in six successive fractions, which were stored in separate tubes, Nos. 2 to 7. Fraction 2 was discarded, as the spectrum showed that but little krypton was present.

The remaining five fractions, Nos. 3 to 7, were submitted to a further fractionation in the following manner. The fraction containing the greatest quantity of argon (3) was introduced into the gasholder and condensed in the bulb. About two-thirds of this was then allowed to evaporate, and the gas transferred to a tube (8); this gas was afterwards discarded. The contents of the next tube (4) were then condensed, along with the residue from 3, and again partially evaporated; this gas formed the second fraction (9) of the next series. This process was repeated with each of the fractions from 3 to 7, the quantities of gas taken off at each fractionation being so graduated that the six resulting fractions (8 to 13) were approximately equal. The last fraction was taken off through the pump, while the liquid air in the jacket was removed so as to make sure that no traces of xenon were lost. By treating the fractions 9 to 13 in the same way, six other fractions (14 to 19), were obtained; of these the first two (14 and 15) were rejected after spectroscopic examination. The numbers indicating the rejected fractions are enclosed in square brackets.

As the four remaining fractions (16 to 19) solidified at the temperature of liquid air, we thought that by mixing the gases with oxygen it might perhaps be possible to obtain a more rapid and complete separation. A single experiment sufficed to convince us that the gain would have to be considerable to compensate for the additional trouble and difficulty in manipulation; the method was therefore abandoned.
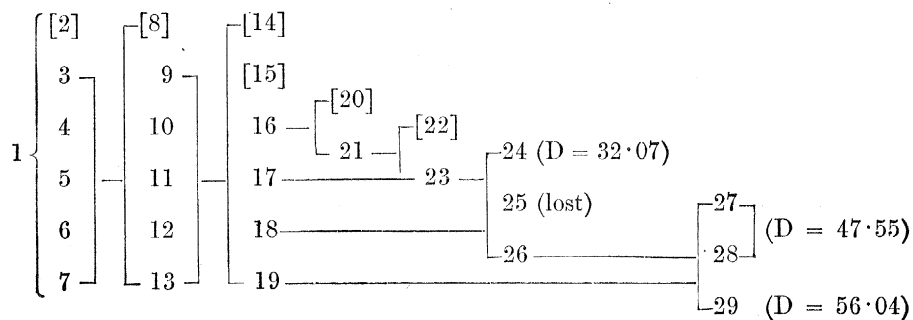
Proceeding by the original method, fraction 16 was condensed, and evaporated in two portions, 20 and 21. The lightest portion (20) amounting to two-thirds of the whole was discarded; the heavier (21) was liquefied together with fraction 17, and divided into a light portion (22), amounting to about one-fifth of the volume of the mixed gases, and a heavier portion (23). In the same way, fractions 24, 25, and 26 were obtained from fractions 18 and 23; and fractions 27, 28, and 29, from fractions 19 and 26.

In the early stages of the fractionation the spectroscope had been the sole guide in

dealing with these gases; but later on, it became evident that we had in our hands gases possessing very different vapour-pressures at the temperature of liquid air; for while argon required additional pressure for its liquefaction, the vapour-pressure of krypton did not exceed 160 millims., and that of xenon appeared to be less than could be measured.

On account of the ease with which these gases solidified, we were obliged to take certain precautions usually unnecessary. If the bulb and stem of the liquefaction bulb were immersed in the liquid air before the introduction of the gas, the gas did not solidify in the bulb but in the stem; and as the liquid air evaporated, it began to volatilise without proper fractionation. To overcome this difficulty, the vacuum vessel was held in a clamp, so that the surface of the liquid air just touched the bottom of the liquefaction bulb, and when the gas was admitted, it condensed in the bulb and not in the tube; the vacuum vessel was then raised so that the liquid air completely covered the bulb. In fractionating krypton and xenon, the fractions of gas were taken off through the pump, as their vapour-pressure was too low to allow of them being collected into the gasholder.

To return to the fractionation of the gases from which the argon was now nearly removed, we had at this point five fractions, viz., Nos. 24, 25, 27, 28, and 29. Fraction 25 was unfortunately lost through an accident; but as the remaining fractions consisted of fairly pure krypton and xenon, and amounted to nearly 50 cub. centims., the loss was not of vital importance. The following table illustrates the method employed in the next series of fractionations.

$$
\begin{array}{ll}
24 \quad (D = 32 \cdot 07) & \left[\begin{array}{l} 30 \\ 31 \end{array}\right] (D = 36 \cdot 6) \\[2em]
\left.\begin{array}{l} 27 \\ 28 \end{array}\right] (D = 47 \cdot 55) & \left[\begin{array}{l} 30 \\ 31 \end{array}\right] (D = 41 \cdot 44) \\[2em]
29 \quad (D = 56 \cdot 04) & \left[\begin{array}{l} 31 \\ 32 \end{array}\right] (D = 61 \cdot 7)
\end{array}
$$
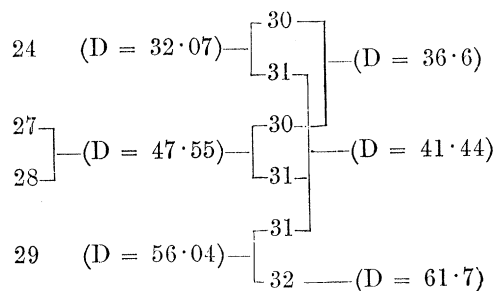
Fractions 27 and 28 were mixed together, and each of the three quantities of gas was in turn solidified in the fractionation bulb, and separated into a lighter and a heavier part. These fractions were mixed as is shown in the table, so as to obtain three samples of gas, two of which appeared from their spectra to be nearly pure krypton; while the third, of density 61·7, consisted chiefly of xenon. The two lighter fractions were separately solidified, and separated into two portions :—

$$
\begin{array}{ll}
(D = 36 \cdot 6) & \begin{array}{l} 33 \text{ (one-third).} \\[0.5em] 34 \text{ (two-thirds)} \quad (D = 40 \cdot 82). \end{array} \\[1em]
(D = 41 \cdot 44) & \begin{array}{l} 35 \text{ (two-thirds)} \quad (D = 40 \cdot 73). \\[0.5em] 36 \text{ (one-third).} \end{array}
\end{array}
$$

The heavier two-thirds of the light gas, and the lighter two-thirds of the heavy gas had the same density.

As the atomic weight of krypton depends upon these determinations, the experimental data are given below :—

	Fraction 34.	Fraction 35.
Volume of bulb . . .	7·152 cub. centims.	7·152 cub. centims.
Weight of gas . . .	0·01515 gramme.	0·01521 gramme.
Pressure	470·6 millims.	474 millims.
Temperature	18·1° C.	18·4° C.
Density	40·82	40·73

The refractivities of the two samples with regard to air were next determined ; they were found to agree within the limits of experimental accuracy :—

Refractivity of fraction 34 . . . . . . 1·450

„ „ 35 . . . . . 1·449

We considered, therefore, that since we had succeeded in separating by fractional distillation from a lighter and from a heavier impurity respectively two samples of gas which agreed in two distinct physical properties, we were justified in assuming that we had isolated a definite chemical substance.

The samples 34 and 35 were mixed, and will from this point be referred to as pure krypton.

The separation of the xenon from traces of krypton proved to be more tedious than difficult ; for though their vapour-pressures at the temperature of liquid air differed considerably, the krypton appeared to remain dissolved in the xenon, and could only be removed by repeated fractionation. Fraction 36, the heavier portion from the last experiment, was introduced into the fractionation bulb, where it of course became solid, and the krypton was allowed to volatilise into the pump, while the exhaustion was continued as long as any gas could be removed. The vessel containing liquid air was then lowered, and the contents of the bulb was pumped off and mixed with fraction 32, the gas of density 61·7 obtained in the previous experiment (p. 65). This operation was repeated several times, with the result that the greater part of the xenon was removed from fraction 36.

Fraction 32 was then submitted several times to the inverse operation. The gas was solidified in the fractionation bulb, which was then placed in connection with the pump and exhausted as far as possible. The liquid air was then removed, and the heavy gas was pumped off and collected ; the operation was repeated, and the gas, after sparking with oxygen to remove traces of nitrogen and carbon compounds, was weighed. Its density was found to be 62·9. After repeating the same operation two or three times the density was again determined :—

Volume of bulb	.	.	.	7·152 cub. centims.
Weight of gas	.	.	.	0·01224 gramme.
Pressure	.	.	.	.	245·4 millims.
Temperature	.	.	.	21·6° C.

The density calculated from these numbers is 64·0.

Unfortunately, after this experiment, a small quantity of air became mixed accidentally with the gas, and lowered the density to 62·96 ; but after refractionation its density was redetermined with the following results :—

Volume of bulb	.	.	.	7·152 cub. centims.
Weight of gas	.	.	.	0·01114 gramme.
Pressure	.	.	.	.	225·3 millims.
Temperature	.	.	.	22·45° C.
Density of xenon	.	.	63·64

The Vapour-pressures of Argon, Krypton, and Xenon.

We have not found it possible to contrive an arrangement whereby the temperature of liquid argon, krypton, and xenon should be gradually altered, as is generally done in measuring the vapour-pressures of substances liquid at the ordinary temperature, by means of a bath of some liquid, the temperature of which can be raised at will, or by jacketing the vapour-pressure tube with vapour from some pure liquid, boiling under different pressures. All substances liquid at the ordinary temperature freeze at the lower temperatures required for these gases. But it is possible to employ liquid ethylene, cooled either by external application of liquid air, or by causing it to boil under reduced pressure ; both these means of obtaining a known low temperature have been used, but only a small range of temperature is thus covered. The results, moreover, were not so trustworthy as those obtained when a liquid of known boiling-point, boiling under atmospheric pressure, was used as a refrigerant.

The plan adopted, therefore, was to determine the pressure corresponding to certain known temperatures, and then by means of the formula suggested by RAMSAY and YOUNG,* the accuracy of which has been demonstrated in a great number of instances, to ascertain the vapour-pressures at intermediate temperatures. This method depends on the fact that the ratios of the absolute temperatures of two liquids corresponding to a series of pressures are a linear function for one of them corresponding to the same pressures. It therefore becomes possible to calculate a whole series of vapour-pressures of any substance, if the pressures are corresponding to two or more temperatures accurately known ; the application is briefly as follows :—

The vapour-pressures of the substances are determined at absolute temperatures

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* ' Phil. Mag.,' vol. 21, p. 33, 1886 ; vol. 22, p. 37, 1886.

T_a, T_a', &c.; and by reference to tables, the absolute temperatures T_b, T_b', &c., for some standard substance, such as water or methyl alcohol, corresponding to the same pressures, are found. The ratios T_a/T_b, T_a'/T_b', &c., are then calculated, and are plotted on curve-paper against the temperatures T_b, T_b', &c., as ordinates. The points so obtained should lie on a straight line, and the temperature corresponding to any particular vapour-pressure can be discovered by multiplying the absolute temperature corresponding to that pressure for the standard substance by the value of the ratio corresponding to that temperature which is read from the line.

For example :—the following result was obtained with krypton—

Pressure.	T_a (krypton).	T_b (CH^3OH).	T_a/T_b.
millims.	Abs.°	Abs.°	
385·6	112·7°	321·8°	0·3502
898·7	123·1	342·3	0·3596
11970·0	170·9	429·3	0·3981
28800·0	197·9	471·4	0·4193

If, now, it is required to calculate the boiling-point of krypton at 760 millims., the ratio is plotted against the values of T_b, and the value of the ratio corresponding to the temperature 338° (the boiling-point of methyl alcohol at normal pressure), is read from the line. It is 0·3578 ; and the product 0·3578 × 338° is the boiling-point of krypton on the absolute scale, 120·9° abs.

This relation is expressed by the formula given by Ramsay and Young :—

$$T_a/T_b = T_a'/T_b' - c(T_a - T_a').$$

The value of c, it will be noticed, is constant for each pair of substances ; and if referred to a standard such as methyl alcohol, the ratio between the values of c for various gases has a physical meaning ; this will be considered later.

The temperatures were based on measurements made with a CALLENDAR's compensated constant-pressure hydrogen thermometer (' Roy. Soc. Proc.,' vol. 50, p. 247) ; in certain cases, a platinum-resistance thermometer, worked in conjunction with a CALLENDAR's recorder, was used ; it had been standardised by help of the hydrogen thermometer ; in others, the hydrogen thermometer was directly employed.

For low pressures, an apparatus was used, the arrangements of which are shown in the annexed figure (fig. 5).

The gas was introduced by means of the inverted siphon into the tube-reservoir a ; this reservoir was in communication with the small bulb b, which in its turn was connected with the pressure-gauge c, and with a TÖPLER's pump through the stop-cock d ; the bulb could be cooled by means of one of the devices previously alluded to. After evacuating the bulb, gauge, and connecting-tubes, the gas was introduced through

the stop-cock at the top of the reservoir; the bulb was cooled; and the pressures were read on the gauge on a mirror-scale, e, parallax being thus avoided.

For high pressures, a pressure-apparatus was made use of, similar to the one depicted in a memoir on Ethyl Oxide, published in the 'Transactions' for 1887 (A, vol. 178, p. 59). The tube containing the gas, however, was bent twice at right-angles, and was a small-bore capillary; for the amounts of gas at our disposal for compression were small (about 3 cub. centims.) because the total volume of the screw displacing the mercury did not admit of the compression of a greater amount; and, moreover, the amount of xenon in our possession was not greater than 3 cub. centims. The end of the capillary tube dipped into the cooling liquid; it was, of course, impossible to measure the volume of the liquefied gas, for care had to be taken to keep the mercury in the compression-tube sufficiently far away from the cold region, in case of its freezing.

Details of Results.—Helium and Neon.—These gases have been liquefied only at the temperature of liquid hydrogen. DEWAR states that helium was liquefied at that temperature under a pressure of eight atmospheres; and our experiments show that even at that temperature, neon possesses a vapour-pressure of a few millimetres. Attempts were made to liquefy neon by compressing it to about 100 atmospheres at the temperature of air boiling *in vacuo* (about − 205°). The pressure rose continuously on decrease of volume, and no liquid could be detected in the tube. The critical temperature of neon, therefore, lies in the unbridged interval between the boiling-point of liquid hydrogen, and that of air under reduced pressure.

Argon.—The lowest temperatures were obtained by the use of liquid nitrogen, boiling in a vacuum-jacket under atmospheric pressure; and the low-pressure apparatus was employed. Liquid air was added from time to time, and the rise of pressure consequent on the rise of temperature was noted. The range was from 77·3° to 87·8° abs.; the pressure from 215 to 821 millims. At the lower tempera-

Fig. 5.
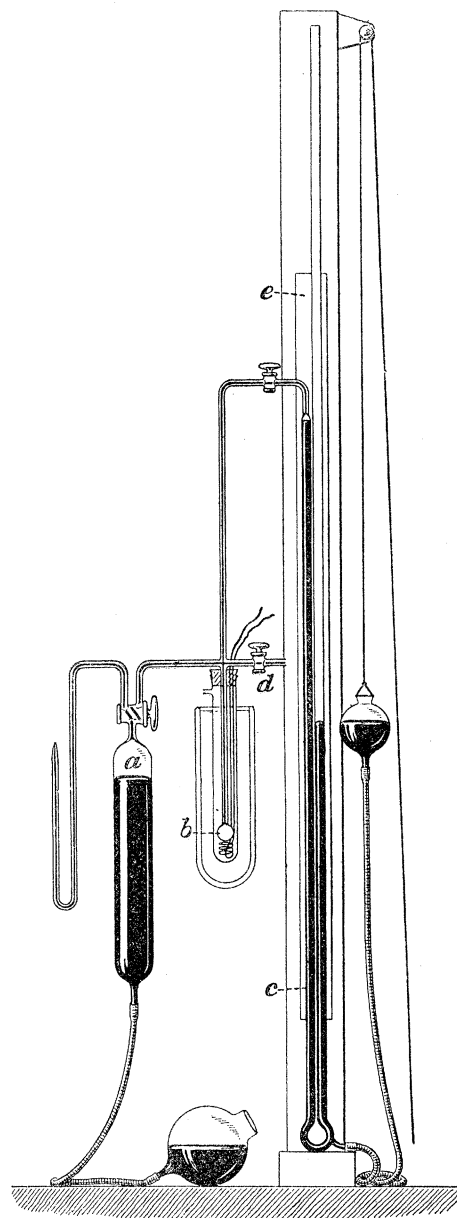
ture, the argon was solid. The temperatures were measured by the resistance of a platinum coil, immersed in the liquid.

For the remaining experiments, the pressure-apparatus was used. The tube was first surrounded by liquid nitric oxide, boiling at 123·1° abs. under atmospheric pressure ; the temperature was measured simultaneously by help of the platinum-resistance thermometer ; the boiling-point of the nitric oxide, a large quantity of which had been prepared and purified by fractional distillation, was previously measured by the hydrogen thermometer. The next temperature was that of ethylene, boiling under reduced pressure ; readings were obtained at 136·8° and at temperatures up to 149° abs. As with nitric oxide, a large quantity of ethylene was prepared, and purified by fractional distillation. The temperatures were here determined with a hydrogen thermometer. Owing to the length of tube immersed in the ethylene, we did not succeed in reading directly the critical temperature, for the mercury froze in the capillary tube. But on using an air-bath (a vacuum-jacket, previously cooled with liquid air), containing the experimental tube, together with the hydrogen thermometer, all being cooled externally by surrounding the inner vacuum-tube with liquid air, the critical change was twice observed, at 155·5° and 155·7° abs. The critical pressure was afterwards determined graphically from the vapour-pressure curve plotted by means of the straight line indicating ratios.

Krypton.—Two observations were made at the temperature of liquid air ; at these temperatures the krypton was solid. The next observation was at the temperature of boiling methane (112·7° abs.), determined as the mean of five experiments with the platinum-resistance thermometer. The boiling-point of nitric oxide (125·1°) gave the next reading ; a further observation was made at the boiling-point of ethylene under atmospheric pressure (170·9°) ; this temperature had previously been determined by the hydrogen thermometer. Lastly, a series of observations was made, using pure dry ether, contained in a vacuum-vessel of half a litre capacity ; the rise of temperature of the ether was very slow, owing to its considerable mass, and to the slow transmission of heat through the walls of the vessel ; and close to the tube were placed the bulb of the hydrogen thermometer and a mechanical stirrer, so that the temperature was nearly uniform throughout. To hasten the rise of temperature, small quantities of ether were introduced from time to time, and two observations were taken at two consecutive temperatures, close together, before adding a fresh dose of warm ether, so as to raise the temperature for the next set of observations. The critical temperature and pressure were also observed.

Xenon.—Observations were made, as before, at the temperature of liquid air, but the vapour-pressure was hardly appreciable. When the temperature of liquid air is alluded to, it must be understood that the thermometer was always used to determine the actual temperature ; and that as the temperature rose owing to the evaporation of nitrogen, fresh observations were made. An attempt was also made

to measure the vapour-pressures of xenon at the boiling-point of nitric oxide and ethylene in the low-pressure apparatus; but the amount of gas at our disposal was insufficient. We had therefore to content ourselves with measurements in boiling nitrous oxide (183·2°; see 'Trans. Chem. Soc.,' vol. 63, p. 836), in cooled ether, and in water. The critical temperature is 14·8° Cent.; and xenon is thus liquefiable at atmospheric temperature.

The results obtained by measurement are as follows:—

VAPOUR-PRESSURES of Argon, Krypton, and Xenon.

	Argon.			Krypton.			Xenon.		
	T. abs.	P.	Ratio.	T. abs.	P.	Ratio.	T. abs.	P.	Ratio.
Temperatures read with platinum thermometer and recorder. Liquid nitrogen mixed with liquid air as a refrigerant.	77·3	215·0	0·2504	84·2	9·0	0·3314	183·2	2020	0·5008
	81·7	410·1	0·2529	88·6	17·4	0·3359	(B. P. of		
	82·1	423·9	0·2536	112·7	386·6	0·3502	N²O).		
	82·4	440·1	0·2537	(B. P. of	—	—	231·4	11134	0·5431
	82·6	465·0	0·2533	CH₄).	—	—	237·4	13505	0·5460
	83·0	485·8	0·2537		—	—	239·7	13971	0·5495
	83·8	524·3	0·2548		—	—	241·2	14696	0·5503
	85·5	633·4	0·2565		—	—	244·2	15868	0·5525
	85·7	644·6	0·2567		—	—	244·6	16301	0·5512
	86·5	704·5	0·2575		—	—	248·7	18153	0·5546
	86·6	716·5	0·2574		—	—	250·5	18929	0·5548
	86·9	757·3	0·2572		—	—	252·6	19984	0·5576
	87·3	787·6	0·2575		—	—	254·0	21512	0·5592
	87·8	821·2	0·2582		—	—	255·6	21967	0·5586
	—	—	—	—	—	—	257·4	22310	0·5615
NO; atmospheric press.	123·1	10306	—	—	—	—	In ether bath, slowly warming; hydrogen thermometer.		
	,,	10322	—	—	—	—			
	,,	10312	0·2910	—	—	—			
Liquid ethylene, boiling under reduced pressure.	136·8	20700	0·3009	170·9	11970	0·3981	273·35	31501	0·5740
	137·8	21334	0·3021	C²H⁴, boiling at atmospheric pressure			In water containing ice, stirred.		
	139·0	23251	0·3019						
				197·9	28808	0·4198	287·75	44112	0·5814
				201·0	30837	0·4229	(Critical temperature and pressure.)		
				201·5	31621	0·4230			
Hydrogen thermometer in air space; pressure read from curve.	155·5	40200	—	204·1	34693	0·4240	In water, stirred.		
	155·7	,,	—	206·4	37006	0·4256			
	(Critical temperature and pressure)			290·5	41245	0·4287			
				(Critical temperature and pressure) Ether bath, slowly warming; hydrogen thermometer.					

On constructing the diagram in which these ratios are mapped against the absolute temperature of methyl alcohol, it was seen that the points representing ratios between the temperatures of the liquid and that of methyl alcohol at the same

pressure bore a linear relation to the absolute temperatures of methyl alcohol. From these results, plotted on a much more open scale, the temperatures of the liquefied gases corresponding to definite pressures were obtained, by finding the temperatures of methyl alcohol corresponding to the same pressures, and reading the ratio corresponding to those temperatures. By multiplying the temperatures of methyl alcohol by the ratios, the temperatures of the liquids at the corresponding pressures were calculated. The following table of vapour-pressures was then constructed (compare Plate 1):—

Pressure.	Temperature.			Pressure.	Temperature.		
	Argon.	Krypton.	Xenon.		Argon.	Krypton.	Xenon.
millims.				millims.			
300	78·94	110·43	148·9	18000	134·88	182·79	248·3
400	81·31	113·84	153·2	20000	137·36	186·00	252·6
500	83·32	116·14	156·8	22000	139·65	188·88	256·6
600	84·89	118·35	159·7	24000	141·80	191·68	260·2
700	86·38	120·19	162·0	26000	143·82	194·32	263·8
760	86·90	121·33	163·9	28000	145·80	196·72	267·2
800	87·77	122·01	164·7	30000	147·58	199·02	270·2
1000	89·90	124·84	168·8	32000	149·28	201·21	273·7
1500	93·52	129·55	176·8	34000	150·88	203·32	276·0
2000	97·95	135·23	182·9	36000	152·52	205·40	278·9
3000	103·33	142·17	192·4	38000	154·11	207·25	281·9
4000	107·27	147·34	199·6	40200	155·60	——	——
6000	113·58	155·47	210·8		Critical		
8000	118·60	161·95	219·6	41240	——	210·5	——
10000	122·72	167·31	226·8			Critical	
12000	126·31	171·87	233·1	43500	——	——	287·7
14000	129·47	175·88	238·7				Critical
16000	132·73	179·45	243·7				

The vapour-pressures of argon were measured for certain temperatures by Professor OLSZEWSKI; the data which he gives are ('Phil. Trans.,' A, 1895, p. 258):—

Pressures.	T. argon.	T. water.	Ratios.	Olszewski. Ratios smoothed.	R. and T. ratios.	Diff.
740·5	86·1	372·27	0·2313	0·2311	0·2337	0·0026
18010	132·9	495·00	0·2705	0·2699	0·2729	30
19230	134·7	498·4	0·2703	0·2710	0·2738	28
20750	136·8	503·4	0·2718	0·2727	0·2754	27
22040	137·9	505·8	0·2726	0·2733	0·2762	29
22650	138·6	507·4	0·2732	0·2738	0·2767	29
27210	143·5	527·8	0·2771	0·2771	0·2800	29
28880	144·4	521·2	0·2771	0·2782	0·2811	29
38460	152·0	538·6	0·2822	0·2834	0·2860	26

On mapping the ratios between the absolute temperatures of water and argon against the absolute temperature of water, a straight line is obtained, which in its slope coincides with that obtained by us. In the table above, we see that the difference between the values of OLSZEWSKI's and our ratios is practically a constant one; and the change of value between $372 \cdot 27°$ and $538 \cdot 6°$ for water is in each case $0 \cdot 0523$. The position of OLSZEWSKI's line is, however, different from ours; and the differences of temperature are shown in the following short table :—

| | Temperatures. | | |
| Pressure. | Olszewski. | | Ramsay and Travers. |
	Observed.	Re-calculated.	
$740 \cdot 5$	$86 \cdot 1$	$86 \cdot 03$	$87 \cdot 00$
18010	$132 \cdot 9$	$133 \cdot 6$	$135 \cdot 1$
19230	$134 \cdot 7$	$135 \cdot 1$	$136 \cdot 5$
20750	$136 \cdot 8$	$137 \cdot 3$	$138 \cdot 6$
22040	$137 \cdot 9$	$138 \cdot 2$	$139 \cdot 7$
22650	$138 \cdot 6$	$138 \cdot 9$	$140 \cdot 4$
27210	$143 \cdot 5$	$143 \cdot 5$	$145 \cdot 0$
28880	$144 \cdot 4$	$145 \cdot 0$	$146 \cdot 5$
38460	$152 \cdot 0$	$152 \cdot 6$	$154 \cdot 0$

It is evident that OLSZEWSKI's temperatures are uniformly below ours; and we imagine that it may be attributed to his having used a constant-volume thermometer, whereas ours was a constant-pressure one. Mr. BALY, who has made measurements of the boiling-points of oxygen and nitrogen with the same thermometer, finds results that also differ from OLSZEWSKI's by $0 \cdot 36°$ for O^2, and by $0 \cdot 15°$ for N^2 in the same direction (higher). On the whole, however, we may take OLSZEWSKI's and our vapour-pressure curves as practically identical, save in the fact that their positions are not quite coincident.

The Molecular Volumes of Argon, Krypton, and Xenon.

The apparatus by means of which the volume of 1 cub. centim. of each of these gases at their boiling-points under atmospheric pressure was measured is shown in the figure (fig. 6).

After the apparatus had been completely exhausted of air through a, which was connected with the pump, the gas was introduced through an inverted siphon, and dried in transit with phosphoric anhydride; when a sufficient quantity had entered, the tube a was sealed. On raising the reservoir b, the volume of the gas

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was read at a known temperature and pressure in the tube c, which had previously been graduated and calibrated. The capillary tube d, which was a piece of even-bore thermometer tubing, was surrounded with a suitable cooling agent, so that the gas was near its boiling-point under normal pressure. By altering the level of b,

Fig. 6.
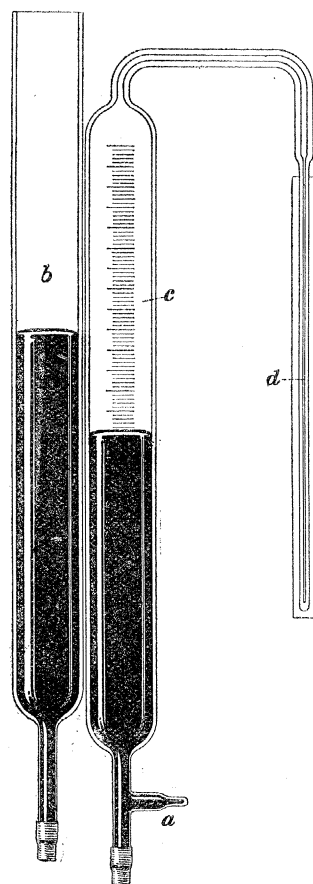
and reading the difference in level of b and c, the actual pressure of the gas was measured. A portion liquefied in d; its volume was read, and also the volume of gas remaining in c, after a portion had been liquefied. As the density of the gas was known, it was easy to calculate the weight of the portion remaining in c, and consequently of the portion liquefied in d.

The volume of one division of the tube c was equivalent to 0.5893 gramme of mercury; that of the capillary d, to 0.000678 gramme. The volume in grammes of mercury from the highest mark on c to the end of the capillary was found by determining the change in volume of the gas in c, consequent on known changes of pressure; and as a mean of five concordant determinations, it was found to be equal to the volume of 6.55 grammes of mercury.

LIQUEFACTION of Argon in Liquid Air.

Argon   D = 19·95.

	Volume of gas uncondensed.	Temp.	Pressure.	Volume at N.P.T.	Volume condensed.	Volume of liquid.	Weight of 1 cub. centim.
1	12·44	15·5	840·2	13·01	23·08	0·03390	1·211
2	10·62	15·2	831·8	11·01	25·08	0·03674	1·214
3	5·43	15·3	816·0	5·52	30·57	0·04474	1·215
4	5·37	15·4	815·7	5·46	30·63	0·04508	1·208
5	5·08	15·6	815·4	5·16	30·93	0·04542	1·211
6	5·61	15·6	818·6	5·72	30·37	0·04461	1·211
	Mean weight of 1 cub. centim. : 1·212 gramme.						

The temperature was about 88° abs., the boiling-point of argon at 760 millims. being 86·9° abs.

LIQUEFACTION of Krypton in Ethylene, cooled below its Boiling-point by being surrounded by Liquid Air.

Krypton   D = 40·78.

	Volume of gas uncondensed.	Temp.	Pressure.	Volume at N.P.T.	Volume condensed.	Volume of liquid.	Weight of 1 cub. centim.
1	20·58	12·8	1298·0	33·57	16·46	0·02820	2·126
2	20·99	,,	1299·7	34·29	15·74	0·02724	2·115
3	21·93	,,	1302·3	35·90	14·13	0·02434	2·115
4	19·46	,,	1295·1	31·68	18·35	0·03044	2·196
5	20·22	,,	1296·4	32·95	17·08	0·02841	2·190
6	20·52	,,	1297·9	33·48	16·55	0·02773	2·174
7	20·75	,,	1298·3	33·88	16·17	0·02705	2·177
8	21·05	,,	1299·8	34·39	15·64	0·02625	2·170
9	21·28	,,	1300·2	34·74	15·25	0·02569	2·162
10	21·78	,,	1302·2	35·80	14·23	0·02434	2·130
	Mean weight of 1 cub. centim. : 2·155 grammes						

The temperature was about 127° abs., the boiling-point at 760 millims. being 121·3° abs.

LIQUEFACTION of Xenon condensed in Ethylene, boiling under Atmospheric Pressure.

Xenon   D = 64·0.

	Volume of gas uncondensed.	Temp.	Pressure.	Volume at N.T.P.	Volume condensed.	Volume of liquid.	Weight of 1 cub. centim.
1	4·95	12·2°	1268·5	15·13	3·96	0·00630	3·59
2	4·85	,,	1268·5	15·03	4·06	0·00644	3·60
3	3·95	,,	1268·5	14·50	4·51	0·00739	3·50
4	3·20	11·7°	1279·4	13·62	5·47	0·00915	3·42

Mean weight of 1 cub. centim. : 3·52 grammes.

The temperature of the xenon was 171° abs.; its boiling-point at 760 millims. is 163·9° abs.

Although these determinations of density have not been made at the actual boiling-points under normal pressure, still they are sufficiently near to show correspondence. The atomic volumes may be obtained by dividing the atomic weights of the elements by their densities. They are :—

$$\text{Argon}: 39\cdot9/1\cdot212 = 32\cdot92.$$
$$\text{Krypton}: 81\cdot55/2\cdot155 = 37\cdot84.$$
$$\text{Xenon}: 128\cdot0/3\cdot52 = 36\cdot40.$$

The Relations between the Volume, Temperature, and Pressure of the Inactive Gases.

The experiments bearing on this question were carried out in an apparatus similar to that of which a figure is given in the 'Phil. Trans.,' A, 1887, p. 59. The volume-tube, carefully calibrated, was charged with a known volume of gas, accurately measured under known conditions of temperature and pressure, and introduced without contamination. The helium was a portion of what had been fractionated by diffusion from any admixture of argon, and it had the density 1·98; the argon was free from helium, neon, krypton, and xenon; they had been removed by fractional distillation; the neon, krypton, and xenon were pure samples of these gases, with densities, 9·97, 40·8, and 64, respectively. Before use, the krypton and xenon were solidified, and freed by the pump from any admixture of gas with higher vapour-pressure.

The method of filling the volume-tube requires special description. It will be understood by reference to the figure (fig. 7).

The volume tube A was sealed with a constriction at B to the apparatus C,

communicating through the stop-cock D with the pump, on the one hand, and through E with the inverted siphon on the other. The point of the siphon was sealed at F, and drawn out to a fine point which was scratched, so that the end could be easily broken by pressing down on it the inverted gas-tube containing the gas under experiment. By raising the reservoir G, mercury entered the apparatus to above the level of the india-rubber tube. The clip K on the india-rubber connecting-tube was then closed. The whole apparatus was then evacuated with the pump, until no bubbles were carried over, an operation lasting half-an-hour. The stop-cocks D, E, and L being shut, the point of the capillary siphon was broken by pressing on it with the inverted test-tube at F, and gas entered the space comprised between the stop-cocks D, E, and L. The stop-cock L was then opened; the gas entered the apparatus, and "washed it out," diluting the residual air (of which there was only the minutest trace, seeing that an almost complete vacuum had been established by the TÖPLER's pump); and this gas was pumped out, and in the case of the rarer gases, collected and preserved. The main body of gas was then admitted by closing D and opening E; and the clip K on the rubber tube was then opened, the mercury reservoir G being temporarily lowered. On raising it again, mercury fell in the reservoir until it took its level in the capillary part opposite B, while the mercury in the volume-tube stood at H. This capillary part of the volume-tube was made of tubing of the same bore as the lower capillary of the reservoir G, so as to avoid errors due to the capillarity of mercury. The temperature and the relative positions on the scale of the levels of the mercury in the capillary tubes and the barometer were then read. The reservoir M was next filled with mercury, and pushed up, until the capillary constriction of the volume-tube at B was well covered. The volume-tube was then bent over, and broken at the capillary B; mercury entered, and

Fig. 7.
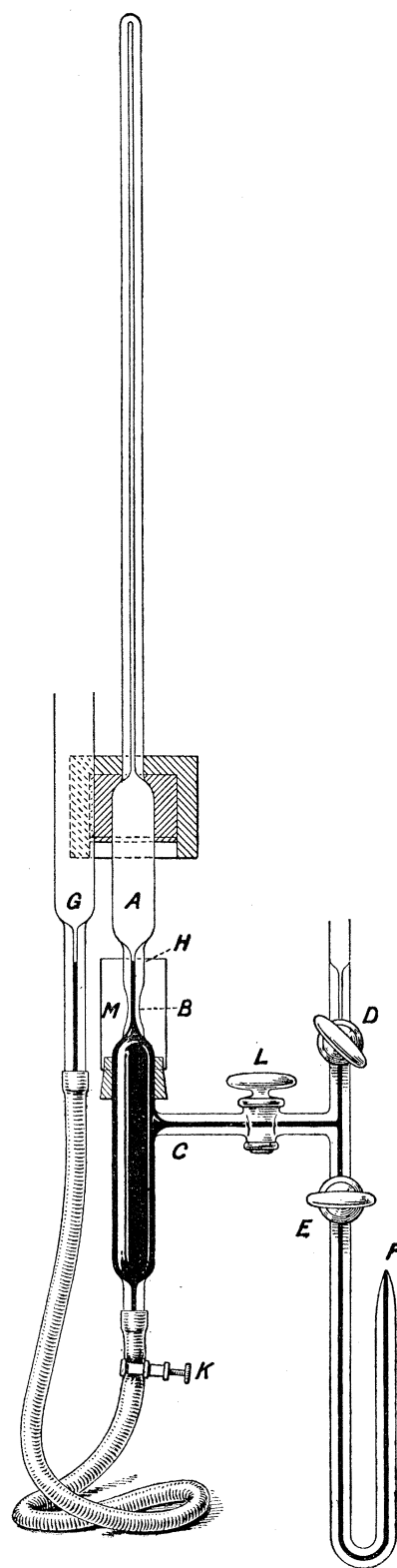
confined a known volume of gas. The volume-tube was transferred to the pressure apparatus, and measurements were made.

The high-pressure manometer had previously been compared with the low-pressure manometer, and the latter, with an open tube manometer. The volume-tube and the high-pressure gauge were jacketed in the first instance with water at atmospheric temperature, which, of course, was accurately known ; and the heights of mercury in the air-gauge and in the volume-tube were read, both during ascending and during descending pressure. The results were quite concordant. The readings of the air-gauge were corrected for deviations from BOYLE's law, according to AMAGAT's results for air, in comparison with directly read pressures ; and the readings of the volume-tube were translated into real volumes, and, by assuming GAY-LUSSAC's law, corrected to what they would have been at $11.2°$ C., which happened to be the temperature at which readings were taken with the gas first investigated, helium. As the highest temperature recorded did not exceed $15°$, it was assumed that no actual variation from GAY-LUSSAC's law would influence the results, within such a small interval of temperature as that between $15°$ and $11.2°$.

For a higher temperature, the boiling-point of quinoline under atmospheric pressure, about $237.3°$, was chosen. The pressure of the atmosphere was not always quite normal ; but the barometer was always read, and the necessary change in volume was calculated according to GAY-LUSSAC's law for the small interval of temperature required—only $0.1°$.

The pressures, volumes, and their products are given in the accompanying tables. The volumes are stated in terms of cubic centimetres occupied by the molecular weight of the gas taken in grammes at the pressures and temperatures specified. They are thus all comparable with each other, and with the corresponding constants for 28 grammes of atmospheric nitrogen, as measured by AMAGAT with a direct-reading manometer. The basis of calculation has been taken as the volume occupied by 32 grammes of oxygen. Data on this constant vary slightly among themselves. The mean of REGNAULT's, RAYLEIGH's, JOLLY's and LEDUC's determinations for the weight of a litre of oxygen is 1.42961 gramme ; that of RAYLEIGH is 1.42952 ; and of LEDUC, 1.42920. Taking RAYLEIGH's number as occupying an intermediate position between the other two, 32 grammes of oxygen would occupy at $0°$ and 760 millims. $22,395$ cub. centims. ; multiplying by 0.760, the normal pressure as a fraction of a metre, the value of P.V. is $17,012$ metre-cubic-centims. At $11.2°$, from GAY-LUSSAC's law, this value is increased to $17,710$; and at $237.3°$, the other temperature under consideration, to $31,800$. On the hypothesis that the products of pressure and volume for a perfect gas remain constant, these values should represent P.V. at all pressures and volumes. We shall now see how far this condition is fulfilled by the gases in question. For the sake of convenient comparison, AMAGAT's results for atmospheric nitrogen have been inserted, both in the tables, and in the diagram (Plate 2) representing the results.

PRESSURE, Volume, and P.V. at Atmospheric Temperature, 11·2° C.

	Nitrogen, 28 grammes.					Helium, 4 grammes.			Neon, 20 grammes.		
	Amagat.		R. and T.								
P.	V.	P.V.	P.	V.	P.V.	P.	V.	P.V.	P.	V.	P.V.
metres.	cub. centims.		metres.	cub. centims.		metres.	cub. centims.		metres.	cub. centims.	
20	—	17595	—	—	—	21·120	825·1	17426	29·870	590·5	17638
25	—	17580	—	—	—	21·962	793·4	17425	31·609	557·6	17626
30	—	17560	—	—	—	22·918	761·6	17455	33·574	523·8	17587
35	—	17548	—	—	17625	23·924	729·3	17448	35·819	491·9	17618
40	—	17539	41·573	423·4	17607	25·070	695·8	17445	38·370	458·4	17588
45	—	17539	45·037	390·9	17548	26·312	663·3	17454	41·322	426·1	17609
50	—	17540	49·146	357·0	17554	27·684	629·7	17431	44·791	392·8	17503
55	—	17549	54·138	324·2	17577	29·317	596·8	17437	48·876	359·4	17564
60	—	17557	60·307	291·5	—	30·918	564·6	17460	53·868	327·7	17652
65	—	17572	—	—	17530	32·833	530·9	17431	57·214	309·6	17714
70	—	17594	68·096	257·4	—	35·013	498·2	17443	59·980	294·2	17643
75	—	17624	—	—	17436	37·499	465·3	17449	64·407	275·4	17739
80	—	17651	79·353	224·8	—	40·377	432·2	17452	67·782	260·7	17673
—	—	—	—	—	—	43·749	399·7	17485	71·458	248·8	17777
—	—	—	—	—	—	47·724	364·8	17408			
—	—	—	—	—	—	52·557	332·3	17466			
—	—	—	—	—	—	58·535	299·3	17523			
—	—	—	—	—	—	66·119	266·9	17647			
—	—	—	—	—	—	77·012	231·9	17859			

At 237·3°.

	Nitrogen, 28 grammes.					Helium, 4 grammes.			Neon, 20 grammes.		
	Amagat.		R. and T.								
P.	V.	P.V.	P.	V.	P.V.	P.	V.	P.V.	P.	V.	P.V.
—	—	—	39·010	826·0	32222	40·956	755·7	30950	33·810	925·9	31304
—	—	—	42·100	766·4	32266	44·329	697·1	30903	36·041	868·0	31285
—	—	—	49·720	648·4	32283	48·347	638·1	30848	38·592	809·1	31226
—	—	—	54·758	589·9	32302	53·206	578·7	30790	41·530	751·1	31193
—	—	—	60·983	530·1	32328	59·238	519·9	30796	44·987	691·0	31086
—	—	—	65·492	494·4	32377	66·929	461·6	30892	49·070	633·7	31094
—	—	—	68·919	471·8	32515	77·884	401·7	31285	54·157	574·9	31136
—	—	—	74·669	434·1	32414	—	—	—	57·381	541·0	31036
—	—	—	76·852	421·3	32378	—	—	—	60·169	517·2	31119
—	—	—	—	—	—	—	—	—	64·582	483·0	31190
—	—	—	—	—	—	—	—	—	68·112	457·9	31187
—	—	—	—	—	—	—	—	—	71·840	433·2	31124

PRESSURE, Volume, and P.V. at Atmospheric Temperature, 11·2° C.

Argon, 39·9 grammes.			Krypton, 81·5 grammes.			Xenon, 164 grammes.		
P.	V.	P.V.	P.	V.	P.V.	P.	V.	P.V.
metres.	cub. centims.		metres.	cub. centims.		metres.	cub. centims.	
—	—	—	19·669	879·2	17166	19·492	771·6	15042
—	—	—	20·405	839·0	17120	20·230	737·2	14913
—	—	—	21·211	811·8	17092	21·040	702·3	14776
—	—	—	22·065	770·5	17000	21·884	667·6	14609
22·945	774·6	17771	23·033	736·5	16965	22·851	632·6	14456
23·947	740·5	17732	24·046	700·8	16851	23·868	595·6	14217
25·097	705·9	17717	25·197	668·4	16841	25·018	560·5	14022
26·316	672·3	17692	26·438	632·7	16728	26·270	525·5	13805
27·686	637·7	17655	27·819	597·7	16629	27·656	490·0	13552
29·214	602·4	17598	29·359	562·8	16523	29·199	452·2	13203
30·935	568·4	17583	31·073	528·3	16416	30·923	417·0	12894
32·854	532·9	17509	32·991	494·1	16302	32·863	378·2	12430
35·012	497·0	17400	35·180	459·2	16157	35·125	339·4	11917
37·497	463·2	17369	37·682	422·8	15934	37·537	300·1	11266
40·358	428·0	17274	40·828	389·3	15895	40·430	234·3	9420
43·722	403·1	17221	43·933	354·3	15564	—	—	—
47·698	357·9	17069	47·933	318·8	15280	—	—	—
52·509	324·4	17033	52·792	283·9	14990	—	—	—
58·479	289·3	16921	54·798	248·9	14633	—	—	—
66·021	255·3	16853	66·420	214·8	14264	—	—	—
76·852	219·7	16889	77·322	180·1	13924	—	—	—

At 237·3°.

P.	V.	P.V.	P.	V.	P.V.	P.	V.	P.V.
—	—	—	38·707	824·8	31924	—	—	—
—	—	—	41·664	765·3	31886	40·681	736·4	30114
44·420	721·8	32060	45·113	704·5	31783	44·061	680·1	29965
48·421	659·8	31949	49·488	644·0	31680	48·042	618·5	29714
53·303	599·2	31940	54·109	583·7	31583	52·915	560·4	29656
59·340	539·3	32001	60·229	523·3	31521	58·927	497·4	29313
66·988	479·9	32150	68·044	462·5	31473	66·997	436·2	29223
77·954	412·7	32174	79·108	402·4	31830	77·935	375·8	29288

ARGON. Repetition at 237·3°.

P.	V	P.V.
32·844	959·1	32460
32·370	899·3	32370
38·511	827·7	32267
44·450	777·6	32233
44·900	715·8	32142
48·880	654·7	32001
53·927	595·3	32103
57·267	560·0	32069
60·047	534·0	32067
64·482	499·7	32222
67·849	474·1	32170
71·542	450·1	32203

These results are graphically reproduced on Plate 2.

Determination of Refractivity.—The apparatus which we employed is essentially the same as that described by Lord RAYLEIGH, in the 'Proceedings,' vol. 59, p. 202, and vol. 64, p. 67, and differed from it only in dimensions. The parallel tubes of the refractivity apparatus were of glass, and had an internal diameter of 2 millims.; their length was 32 centims.; the gauge-tubes were 4 millims. in diameter, and the connecting tubes were of capillary bore; and the total capacity at full pressure was 5 cub. centims., but it was possible to work with 3 cub. centims. of gas. The focal length of the lenses was 30 centims.

The refractivity was determined in the manner previously described.

Helium . . . . 0·1238
Neon . . . . (I.) (0·235; II.) 0·234 . . . . . . 0·2345
Argon . . . . 0·968
Krypton . . . . . (I.) 1·450; (II.) 1·449 . . . . . . 1·450
Xenon . . (I.) 2·361; (II.) 2·365; (III.) 2·379; (IV.) 2·352 . 2·364

The refractivity of helium and argon were previously determined ('Proc. Roy. Soc.,' vol. 64, p. 190); that of neon was compared with hydrogen; and the refractivity of hydrogen compared with air was found equal to 0·4733 ('Proc. Roy. Soc.,' vol. 62, p. 227).

Two samples of krypton were obtained, one by fractionating from argon (I.);

the other after fractionating it from xenon (II.). The ratio between the refractivities of (I.) and (II.) were 1·003 to 1 ; the mean of all observations is 1·450.

Spectra of the Inactive Gases.

It is not intended to give a complete account of the spectra of the inactive gases ; exceedingly accurate measurements have been made by Mr. E. C. C. BALY, with a ROWLAND's grating, which will shortly be published. But to the general reader, it is of interest to gain some idea of the visual spectra, and these have been reproduced in Plate 3 from drawings made under the supervision of Professor ERDMANN, from tubes furnished to him by us.

The spectra of neon, krypton, and xenon cannot be detected in that of crude argon, even by photographic methods.

The change of spectrum produced in argon by the introduction of a jar and spark-gap is well known ; but less attention has been paid to the fact that helium, too, alters its spectrum, though much less markedly. The effect of the jar and spark-gap with krypton is almost to obliterate the spectrum ; the brilliant yellow and green lines disappear. The spectrum of neon is hardly changed ; but that of xenon is enormously intensified ; indeed the plate shows the jar and spark-gap spectra of xenon. With the ordinary discharge, it is far less luminous, and the blue lines become only faintly visible ; the blue and green are much intensified by the interposition.

The colour of these tubes is very striking ; the yellow of helium and the red-purple of argon are now well known ; neon has a brilliant flame-colour, as intense as the yellow of helium ; krypton has a pale violet tint, and is not striking ; and xenon is sky-blue, and with the jar acquires a greener tint.

The question of the identity of the spectrum of krypton and that of the aurora borealis can be settled after the publication of Mr. BALY's work.

Conclusions, and Résumé of Results.

The densities of the inactive gases are respectively :—

Helium.	Neon.	Argon.	Krypton.	Xenon.
1·98	9·96	19·96	40·78	64·0

There are two lines of argument which show that these numbers, multiplied by 2, give approximately the atomic weights of the elements.

(1.) The ratio between their specific heats at constant pressure and at constant volume is 1·66. It is true that no measurements have been made with pure neon,

krypton, and xenon, yet many determinations by the Kundt method were carried out with the approximately pure gases. It is hardly necessary to point out that if the theoretical ratio of 1·66 is attained with a mixture of monatomic gases, it applies also to the constituents of that mixture. This reasoning supports the above assertion.

(2.) Supposing that the atomic weights, as in the case of oxygen, nitrogen, &c., be taken as identical with the numbers expressing density, there is no place for these elements in the periodic table. This argument, of course, does not necessarily apply to helium, for it occupies the gap between hydrogen (1) and lithium (7). But neon would occupy a place between beryllium (9) and boron (11); argon between fluorine (19) and sodium (23), taking the place we have assigned to neon; krypton between calcium (40) and scandium (44); and xenon, between copper (63·6) and zinc (65·4). But if it be granted that they are monatomic, they form a group by themselves. Their atomic weights would then be:—

Helium.	Neon.	Argon.	Krypton.	Xenon.
4	20	40	82	128

The group of elements, the atomic weights of which come next in order, is:—

Hydrogen.	Helium.	Lithium.	Beryllium.
1	4	7	9
Fluorine.	Neon.	Sodium.	Magnesium.
19	20	23	24
Chlorine.	Argon.	Potassium.	Calcium.
35·5	40	39	40
Bromine.	Krypton.	Rubidium.	Strontium.
80	82	85	87
Iodine.	Xenon.	Cæsium.	Barium.
127	128	133	137

It may appear remarkable that hydrogen is placed as the first member of the chlorine-group; but arguments may be adduced in favour of this position, which need not be here recapitulated, and which have been well summed-up by Professor ORME MASSON ('Chem. News,' vol. 73, 1896, p. 283). It is also to be noticed that the group ends here; for no elements of the fluorine, sodium, and magnesium series with higher atomic weights than iodine, cæsium and barium have been discovered. We have no absolute proof that "xenon" does not contain some element of still higher weight; the same could have been said of argon at the time of publication of the 'Phil. Trans.' memoir; but it may be confidently stated that if xenon contains elements of higher atomic weight, they must be present in an extremely minute amount; inasmuch as the pressure does not rise during the process of its condensation

to liquid ; and the critical phenomena are sharp. This is known not to be the case with a mixture. Our opinion is that this portion of the table is complete.

We have next to show that the properties of these elements vary periodically, like those of the cognate elements.

Refractivities.—The found refractivities of the inactive gases compared with air as unity are :—

Helium.	Neon.	Argon.	Krypton.	Xenon.
0·124	0·235	0·968	1·450	2·368

We see here a progressive increase with atomic weight.

The following table gives a résumé of the refraction-equivalents of the elements, taken from the summary in OSTWALD's 'Allgemeine Chemie,' vol. 1, p. 447 ; the refractivities of the inactive gases have been calculated to the same basis as those of the other elements :—

Hydrogen.	Helium.	Lithium.	Beryllium.	Boron.	Carbon.	Nitrogen.	Oxygen.
1·47	0·47	3·8	4·0	4·0	5·0	4·1	3·5

Fluorine.	Neon.	Sodium.	Magnesium.	Aluminium.	Silicon.	Phosphorus.	Sulphur.
1·4	0·89	4·2	7·0	8·4	7·5	18·3	16·0

Chlorine.	Argon.	Potassium.	Calcium.	Scandium.	Titanium.	Vanadium.	Chromium.
10·0	3·68	8·1	10·4	——	25·5	25·3	19·9

Manganese.	Iron. 12·0 / Nickel. 10·4 / Cobalt. 10·8	Copper.	Zinc.	Gallium.	Germanium.	Arsenic.	Selenium.
12·2		11·6	10·2	——	——	15·4	30·5

Bromine.	Krypton.	Rubidium.	Strontium.	Yttrium.	Zirconium.	Niobium.
15·3	5·51	14·0	13·6	—	21·0	—

Rhodium. 24·2 / Palladium. 22·4	Silver.	Cadmium	Indium.	Tin.	Antimony.	Tellurium.
	13·0	13·6	—	27·0	24·5	21·6

Iodine.	Xenon.	Cæsium.	Barium.	....
24·5	9·0	19·5	15·8	

Of these, hydrogen, chlorine, bromine, nitrogen, and oxygen, are, with the exception

of the inactive gases, the only elements of which the refractivities have been measured directly; the other refraction-equivalents are deduced from measurements with compounds of the elements.

These figures have been plotted on the accompanying curve; the ordinates are atomic weights, and the abscissæ, the refraction-equivalents. It is noticeable that those of helium, neon, argon, krypton, and xenon form the lower apices of each series. It must of course be understood that many of the numbers for the other elements are far from accurate; still the diagram is interesting inasmuch as it shows clearly the

Fig. 8.

Atomic Weights.
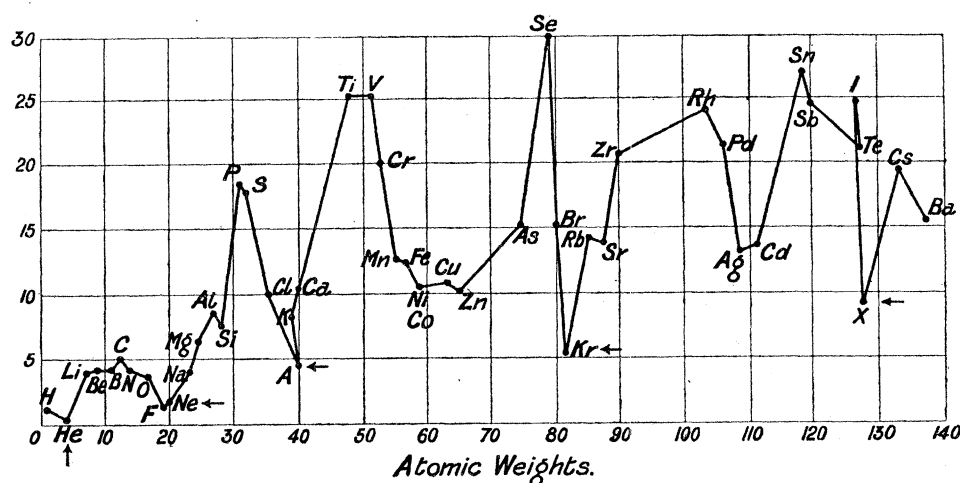
periodicity of the property, and carries with it the conviction that the inactive gases find a fitting place among the other elements.

The comparative retardation of light caused by equal numbers of molecules of the inactive gases compared with that produced with air is given by the figures on p. 84; on dividing by the atomic weights the retardation for equal quantities of matter is arrived at :—

Helium.	Neon.	Argon.	Krypton.	Xenon.
0·0309	0·0118	0·0242	0·0177	0·0184

It is remarkable that if, for example, krypton be submitted to such a pressure that its density is equal to that of xenon at atmospheric pressure, it offers nearly equal opposition to the passage of light, a fact which is highly suggestive, when the ultimate nature of these gases is considered.

Somewhat similar relations are found with the neighbouring series of elements if their values are reduced to the scale of air as unity. The refractivities are far less certain, and the results must be accepted with caution; but the figures are :—

Hydrogen.	Fluorine.	Chlorine.	Bromine.	Iodine.
0·473	0·05 ?	0·073	0·048	0·048

Lithium.	Sodium.	Potassium.	Rubidium.	Cæsium.
0·13	0·048	0·051	0·036	0·038

Compressiiblities.—On referring to the plate (Plate 2) it will be seen that at the lower temperature, 11·2°, the value of P.V. for a perfect gas is 17,710 metre-cubic-centims. The values for nitrogen are taken from AMAGAT's results, and they deviate very little from the theoretical. The compressibility of helium decreases with rise of pressure, or in other words the value of P.V. increases. This is also the case with hydrogen, though in a less degree. Neon is a more perfect gas than nitrogen, though at high pressures, it, too, becomes too little compressible. Argon, on the other hand, is more compressible than the former, and krypton still more ; though the shape of the curve indicates that at still higher pressures their P.V. would become normal at some point. Xenon is below its critical temperature, and its compressibility is therefore very great.

At higher temperatures the results are difficult to interpret. Measurements made with nitrogen show that it retains nearly a uniform P.V. as pressure rises ; but of all the other gases the P.V. diminishes and then increases. And the order of position of the curves is not in accordance with the densities of the gases. That the measurements are fairly correct may be inferred from the two sets for argon being nearly identical. Although these observations at a high temperature cannot be taken as of great importance in themselves, yet they show the necessity of a careful comparison of the behaviour of diatomic gases as regards their compressibility.

The results of the measurements are reproduced on Plate 2.

Vapour-pressures.—As already remarked, it was found impossible to liquefy neon, except by the aid of liquid hydrogen ; and as the constants for hydrogen are unknown, it was useless to attempt a measurement of its vapour-pressure. The same remarks apply to helium. The diagram shows that the vapour-pressure curves of the remaining three elements exhibit a gradual progression.

Using the formula of RAMSAY and YOUNG, as described on p. 68, the ratios between the absolute temperatures of these liquids, and that of methyl alcohol at equal pressures for all are expressible by straight lines, when mapped against the absolute temperature of the alcohol. The slope of such a line affords a physical constant, which is peculiar to each substance. The values of $\Delta R/\Delta t$ for the three elements, argon, krypton and xenon, are :—

Argon.	Krypton.	Xenon.
0·0350	0·0467	0·0675

Here again a progression is noticeable ; it does not, however, appear to be possible to

extrapolate the results, and so to obtain means of calculating the vapour-pressure curves of neon and helium.

Melting-points, Boiling-points and Critical Temperatures.—During the determination of the vapour-pressures and the atomic volumes of argon, krypton, and xenon, we have frequently solidified these elements. The melting-points are as follows :—

Argon.	Krypton.	Xenon.
—187·9° C.	—169° C.	—140° C. (approx.)
85·1° abs.	104° abs.	133° abs.

The melting-point of argon was determined by aid of a platinum thermometer immersed in liquid air ; that of krypton in liquid methane ; and that of xenon in ethylene cooled below its boiling-point. As already mentioned, the temperatures are reduced to the hydrogen standard ; a portion of the vapour-pressure curve of solid krypton was measured, but only two points were obtained, viz., at 9·00 and at 17·4 millims. pressure. The ratios calculated from these two points and plotted on curve-paper, cuts the line representing the ratios for the vapour-pressures of the liquid at a point representing the ratio for the melting-point ; it corresponds to the temperature —166·6° C., a fairly near concordance with the found number —169° C. (See RAMSAY and YOUNG, 'Trans. Chem. Soc.,' vol. 49, p. 460.)

The boiling-points at 760 millims., calculated by the method of ratios, are :—

Argon.	Krypton.	Xenon.
—186·1° C.	—151·67° C.	—109·1° C.
86·9° abs.	121·33° abs.	163·9° abs.

The critical temperatures and pressures are :—

	Argon.	Krypton.	Xenon.
Temperatures . .	—117·4° C.	—62·5° C.	+14·75° C.
	155·6° abs.	210·5° abs.	287·75° abs.
Pressures. . . .	40,200 millims.	41,240 millims.	43,500 millims.

The boiling-point and melting-points of the inactive elements also show periodicity ; it has not been deemed necessary, however, to insert diagrams illustrative of this. Suffice it to remark that these constants place the elements at the bottom of the descending point of such a curve as accompanies LOTHAR MEYER's ' Modern Theories of Chemistry ;' and that here, too, they fall into place.

Atomic Volumes.—So far as is known, the following table gives the atomic volumes at their boiling-points of the elements of interest in connection with those of the argon group.

Nitrogen.*	Oxygen.*	Hydrogen. 14·3 Fluorine.*	Helium. ? Neon.	Lithium. ?(11·9) Sodium.†
17·7	14·1	17·15	?	31·0 (23·7)
Phosphorus.† 20·9 (17·0)	Sulphur.† 21·6 (15·7)	Chlorine.* 23·5	Argon. 32·9	Potassium. ? (45·4)
Arsenic. — (13·2)	Selenium. — (18·5)	Bromine.† 27·1 (26·9)	Krypton. 37·8	Rubidium. ? (56·1)
Antimony. — (17·9)	Tellurium. — (20·3)	Iodine.* 34·2 (25·7)	Xenon. 36·4	Cæsium. ? (70·6)

The figures in brackets refer to atmospheric temperature, and are taken from C. SCHMIDT's work. It is to be noticed, if these figures are mapped as ordinates against atomic weights as abscissæ, as shown by LOTHAR MEYER, that argon follows chlorine on the ascending branch, of which the highest member is potassium; that krypton occupies a regular position on the curve of which the members with lowest atomic volume are cobalt and nickel and the highest rubidium; while the position of xenon is near that of iodine, and lies between it and cæsium. In short, the atomic volumes of these elements exhibit that partial regularity characteristic of all the others; and their place on the atomic volume curve is a normal one.

If it is permissible to speculate on the atomic volumes of helium and of neon by interpolation, they are respectively 13·5 and 20·2. This would make the densities of the liquids 0·30 and 1·0, approximately. These numbers would then complete the following series of densities:—

| Helium.	Neon.	Argon.	Krypton.	Xenon.
0·3 ?	1·0 ?	1·212	2·155	3·52

The whole table of atomic volumes, as far as that of cæsium, is reproduced in the accompanying diagram. The periodicity of the inactive elements is obvious. A word may be said regarding the apparently abnormal position of argon; with the atomic weight 40, there is a reversal of direction in passing from argon to potassium, and from potassium to calcium; but the same peculiarity is observable with iodine and tellurium. While the difference between the atomic weight of any element and that preceding it or succeeding it on the table is generally positive, although very irregular, it appears that a few instances of reversal cannot be ignored, and argon forms one of these. The peculiarity of the diagram, it must be noted, is due to the atomic weight of argon and not to its atomic volume.

* DRUGMAN and RAMSAY, 'Trans. Chem. Soc.,' vol. 67, p. 1228.

† RAMSAY, *ibid.*, vol. 39, p. 472; RAMSAY and MASSON, *ibid.*, vol. 39, p. 49; THORPE, *ibid.*, vol. 37, p. 391.
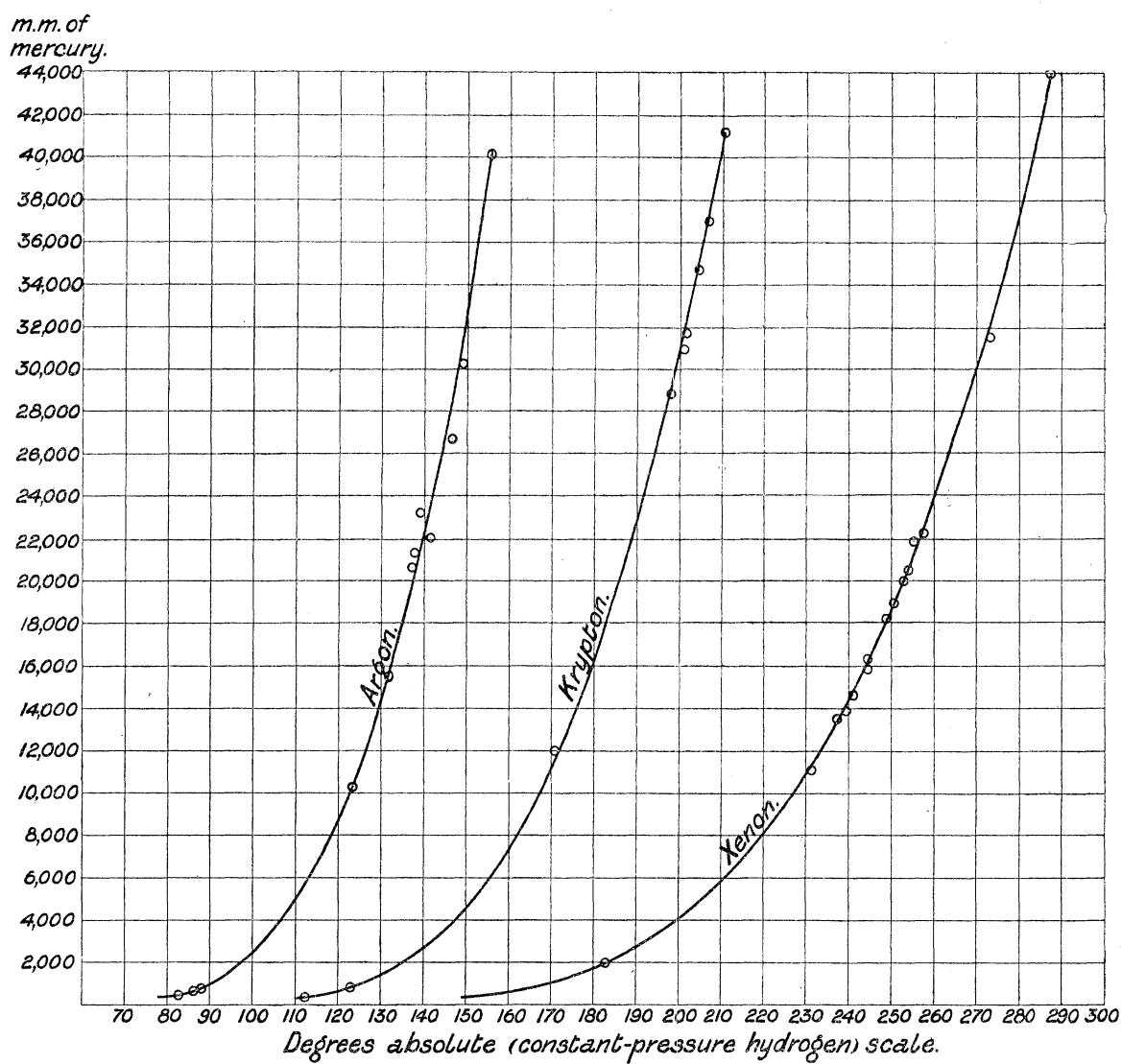
General Remarks.—The great value of Newland's, Mendeléef's, and Lothar Meyer's generalisation, known as the periodic arrangement of the elements, is universally acknowledged. But a study of this arrangement, it must be allowed, is a somewhat tantalising pleasure; for, although the properties of elements do undoubtedly vary qualitatively, and, indeed, show approximate quantitative relations to their position in the periodic table, yet there are inexplicable deviations from regularity, which hold forth hopes of the discovery of a still more far-reaching generalisation. What that generalisation may be is not yet to be divined; but that it must underlie what is known, and must furnish a clue to the explanation of irregularities, cannot be disputed.
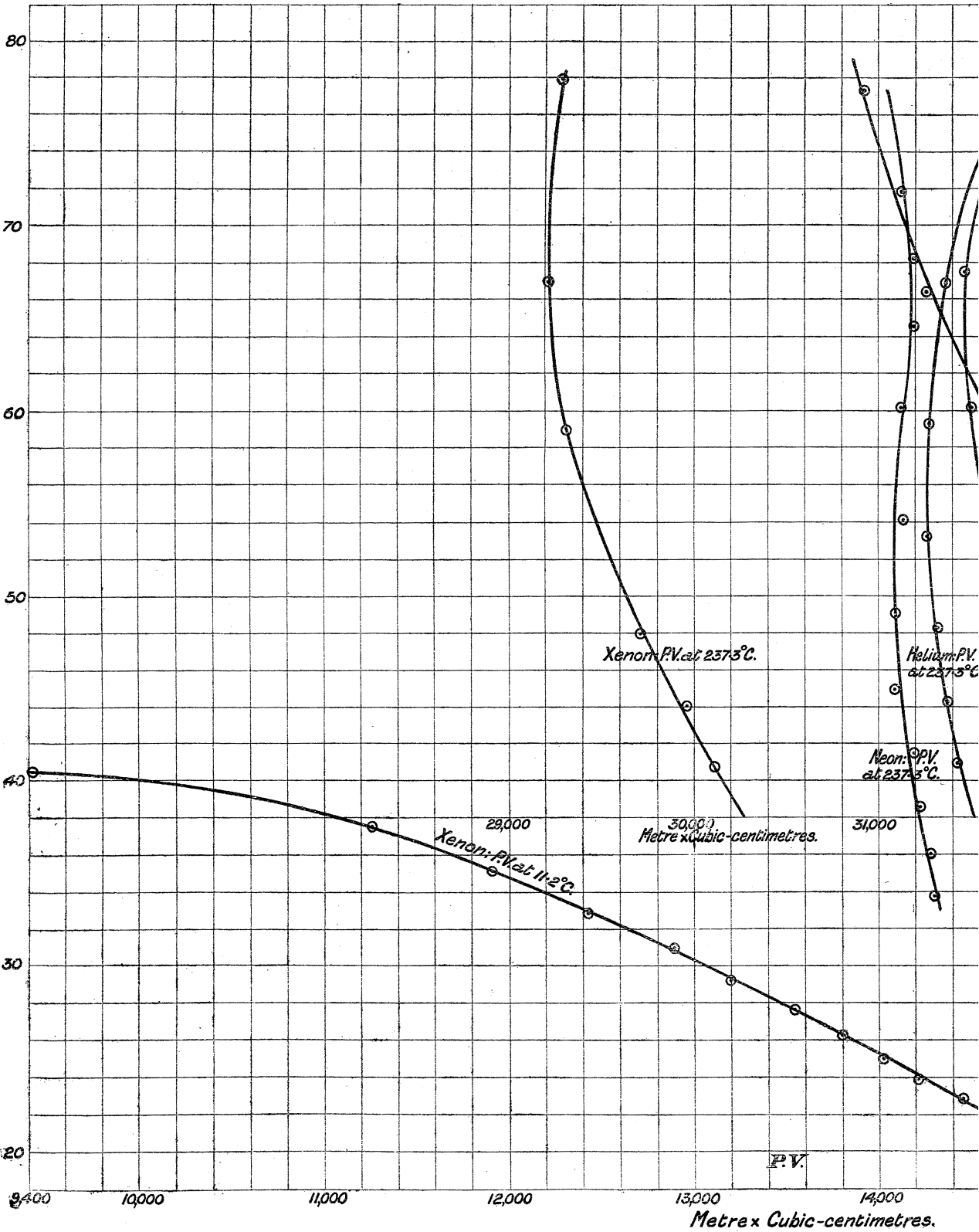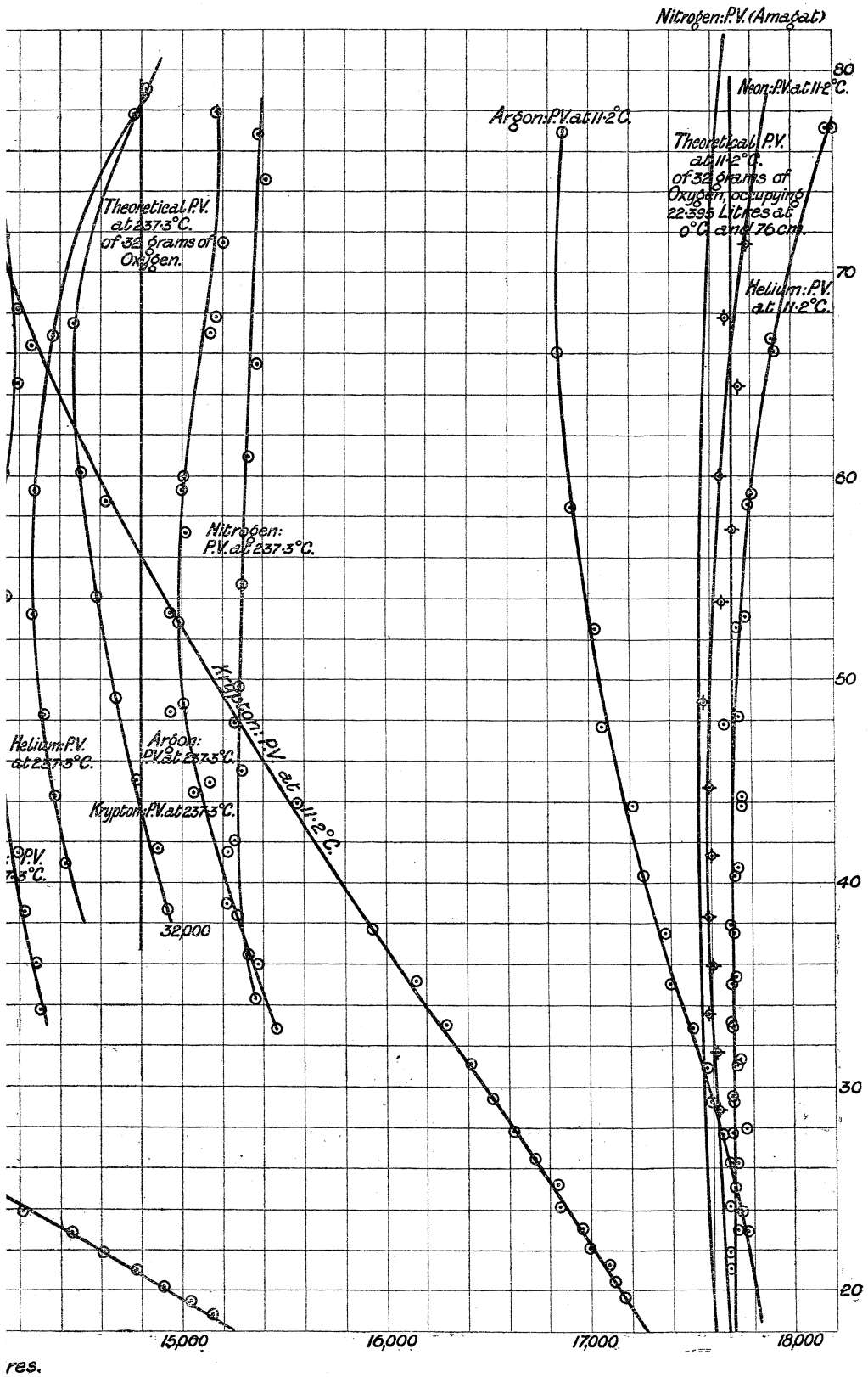
Fig. 9.

Atomic Weights.
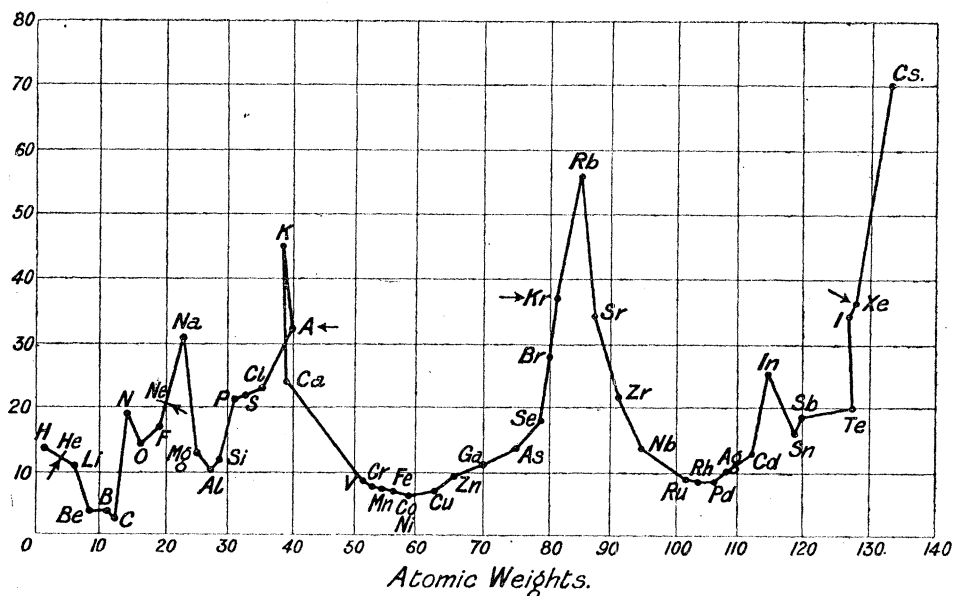
When we began the search for the elements of which the physical properties are described in the foregoing pages, we were not without a strong hope that their discovery would solve the problem. For there can be little doubt that these inactive elements constitute simple, if not the simplest forms of matter. They have no tendency to form compounds, and are monatomic; their physical relations, we may therefore presume, are not subject to interference by the simultaneous exercise of chemical functions. But our hope has been fruitless. While the same rough quantitative correspondence between the order in the periodic table and the physical properties is manifest, as with other similar series of elements, we have failed to trace any simple mathematical expressions which would make it possible to predict with accuracy the physical properties of any one of these elements, from a knowledge of those of its congeners. It is possible that such expressions exist; we venture to hope that others, more mathematically gifted than we are, may succeed where we have failed.
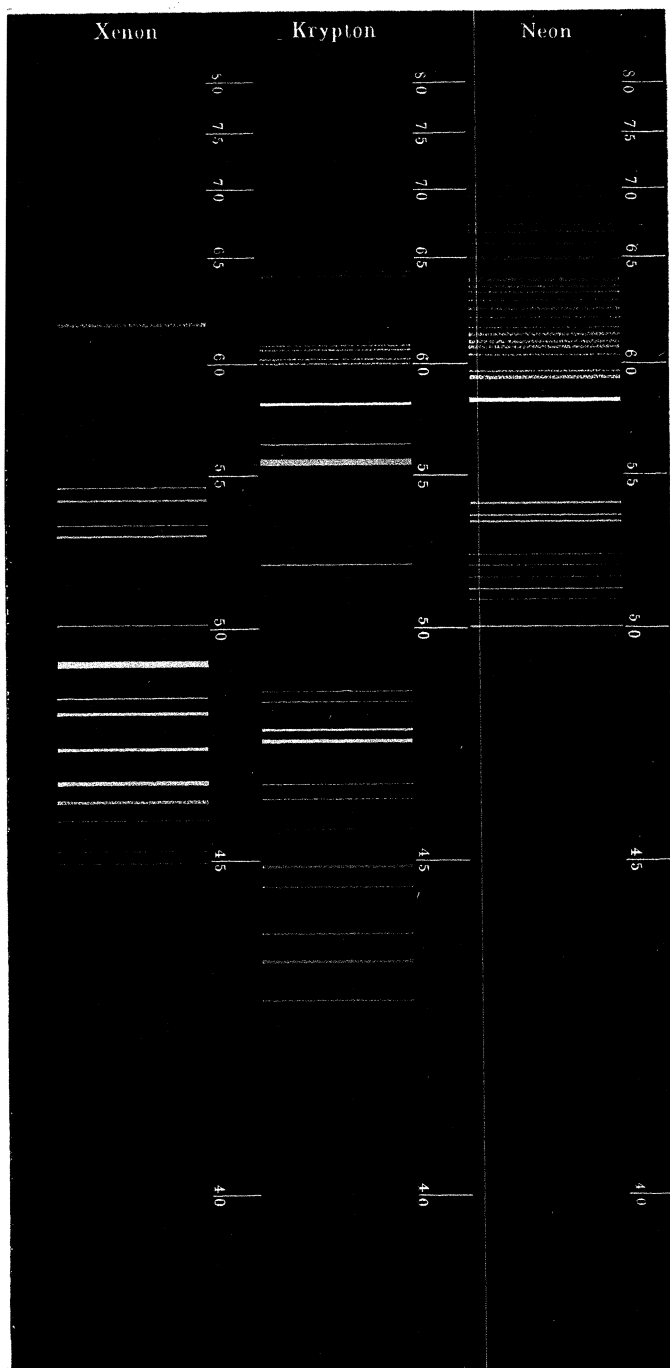
Ramsay and Travers.

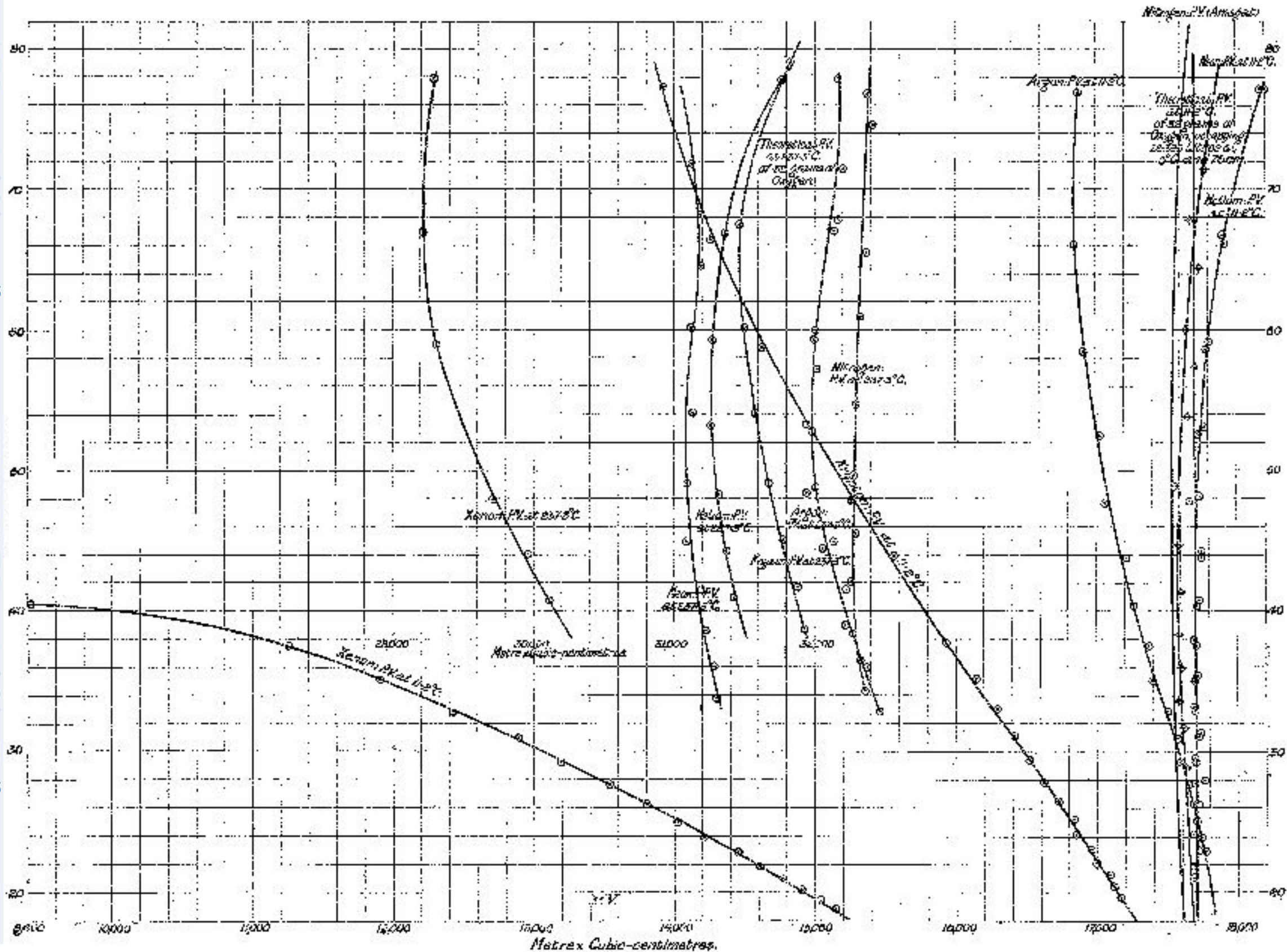*Phil. Trans., A, vol.* 197, *Plate* 1.

Degrees absolute (constant-pressure hydrogen) scale.

80

70

60

50

40

30

20

Xenon: P.V. at 237.3°C.

Xenon: P.V. at 11.2°C.

Helium: P.V. at 237.3°C.

Neon: P.V. at 237.3°C.

29,000   30,000   31,000
Metre × Cubic-centimetres.

P.V.

9,400   10,000   11,000   12,000   13,000   14,000

Metre × Cubic-centimetres.

Nitrogen: P.V. (Amagat)

Neon: P.V. at 11·2°C.

Argon: P.V. at 11·2°C.

Theoretical. P.V. at 11·2°C. of 32 grams of Oxygen, occupying 22·395 Litres at 0°C. and 76 cm.

Theoretical. P.V. at 237·3°C. of 32 grams of Oxygen.

Helium: P.V. at 11·2°C.

Nitrogen: P.V. at 237·3°C.

Krypton: P.V. at 11·2°C.

Helium: P.V. at 237·3°C.

Argon: P.V. at 237·3°C.

Krypton: P.V. at 237·3°C.

32,000

15,000   16,000   17,000   18,000

res.

Xenon   Krypton   Neon