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The density of gases in the air and the discovery of argon

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The subject of the densities of gases has engaged a large part of my attention for over 20 years. In 1882 in an address to the British Association I suggested that the time had come for a redetermination of these densities, being interested in the question of Prout's law. At that time the best results were those of Regnault, according to whom the density of oxygen was 15.96 times that of hydrogen. The deviation of this number from the integer 16 seemed not to be outside the limits of experimental error.

In my work, as in the simultaneous work of Cooke, the method of Regnault was followed in that the working globe was counterpoised by a dummy globe (always closed) of the same external volume as itself. Under these conditions we became independent of fluctuations of atmosphere density. The importance of this consideration will be manifest when it is pointed out that in the usual process of weighing against brass or platinum weights, it might make more apparent difference whether the barometer were high or low than whether the working globe were vacuous or charged with hydrogen to atmospheric pressure. Cooke's result, as at first announced, was practically identical with that of Regnault, but in the calculations of both these experimenters a correction of considerable importance had been overlooked. It was assumed that the external volume of the working globe was the same whether vacuous or charged to atmospheric pressure, whereas of course the volume must be greater in the latter case. The introduction of the correction reduced Cooke's result to the same as that which I had in the meantime announced, viz. 15.88. In this case therefore the discrepancy from Prout's law was increased, and not diminished, by the new determination.

Turning my attention to *nitrogen*, I made a series of determinations, using a method of preparation devised originally by Harcourt, and recommended to me by Ramsay. Air bubbled through liquid ammonia is passed through a tube containing copper at a red heat where the oxygen of the air is consumed by the hydrogen of the ammonia, the excess of the ammonia being subsequently removed with sulphuric acid. In this case the copper serves

merely to increase the surface and to act as an indicator. As long as it remains bright, we have security that the ammonia has done its work.

Having obtained a series of concordant observations on gas thus prepared I was at first disposed to consider the work on nitrogen as finished. Afterwards, however, I reflected that the method which I had used was not that of Regnault and that in any case it was desirable to multiply methods, so that I fell back upon the more orthodox procedure according to which, ammonia being dispensed with, air passes directly over red hot copper. Again a series in good agreement with itself resulted, but to my surprise and disgust the densities obtained by the two methods differed by a thousandth part - a difference small in itself but entirely beyond the experimental errors. The ammonia method gave the smaller density, and the question arose whether the difference could be attributed to recognized impurities. Somewhat prolonged inquiry having answered this question in the negative, I was rather at a loss how to proceed. It is a good rule in experimental work to seek to magnify a discrepancy when it first presents itself, rather than to follow the natural instinct of trying to get quit of it. What was the difference between the two kinds of nitrogen? The one was wholly derived from air; the other partially, to the extent of about one-fifth part, from ammonia. The most promising course for magnifying the discrepancy appeared to be the substitution of oxygen for air in the ammonia method, so that *all* the nitrogen should in that case be derived from ammonia. Success was at once attained, the nitrogen from the ammonia being now 1/200 part lighter than that from air, a difference upon which it was possible to work with satisfaction. Among the explanations which suggested themselves were the presence of a gas heavier than nitrogen in the air, or (what was at first rather favoured by chemical friends) the existence in the ammonia-prepared gas of nitrogen in a dissociated state. Since such dissociated nitrogen would probably be unstable, the experiment was tried of keeping a sample for eight months, but the density was found to be unaltered.

On the supposition that the air-derived gas was heavier than the "chemical" nitrogen on account of the existence in the atmosphere of an unknown ingredient, the next step was the isolation of this ingredient by absorption of nitrogen. This was a task of considerable difficulty; and it was undertaken by Ramsay and myself working at first independently but afterwards in concert. Two methods were available - the first that by which Cavendish had originally established the identity of the principal component of the atmosphere with the nitrogen of nitre and consisting in the oxidation of the

nitrogen under the influence of electric sparks with absorption of the acid compounds by alkali; the other method was to absorb the nitrogen by means of magnesium at a full red heat. In both these ways a gas was isolated of amount equal to about one per cent of the atmosphere by volume and having a density about half as great again as that of nitrogen. From the manner of its preparation it was proved to be non-oxidizable and to refuse absorption by magnesium at a red heat, and further varied attempts to induce chemical combination were without result. On this account the name *argon* was given to it. The most remarkable feature of the gas was the ratio of its specific heats, which proved to be the highest possible, viz. 1.67, indicating that sensibly the whole of the energy of molecular motion is translational.

Argon must not be deemed rare. A large hall may easily contain a greater weight of it than a man can carry.

In subsequent investigations Ramsay and Travers discovered small quantities of new gases contained in the aggregate at first named argon. Helium, originally obtained by Ramsay from cleveite, is also present in minute quantity.

Experiments upon the refractivity and viscosity of argon revealed nothing specially remarkable, but the refractivity of helium proved to be unexpectedly low, not attaining one-third of that of hydrogen - the lowest then known.

As regards the preparation of argon, it is advantageous to begin with *liquid air*, for preparing which a plant is now to be found in many laboratories. It should perhaps be remarked that "liquid air" is something of a misnomer. What is liquified is not the whole of the air supplied or even a fair sample of it. The oxygen, being less volatile, is contained in undue proportion, and this excess increases as evaporation proceeds. Argon, being intermediate in volatility, may be expected to increase relatively to the nitrogen, though it decreases relatively to the oxygen. A number of analyses for oxygen and argon as evaporation proceeded are appended (Table 1); they relate to the *vapour* arising from the liquid and not to the liquid itself. The oxygen, expressed as a fraction of the whole, varied from 30 to 98 per cent. From 43 to 90 per cent of oxygen, the argon, as a percentage of the whole, scarcely varied from 2.0.

The experiment under the head 98 per cent is not quite comparable with the others. The last entry, corresponding to 100 per cent of oxygen, is theoretical and does not represent any actual experiment.

Table 1.

<i>Percentage of oxygen</i>	<i>Percentage of argon</i>	<i>Argon, as a percentage of nitrogen and argon</i>
30	1.3	1.9
43	2.0	3.5
64	2.0	5.6
75	2.1	8.4
90	2.0	20.0
98	0.76	33.0
100	0.00	100.0

The above numbers show that a great advantage may be obtained by starting with liquid air. Something depends upon the procedure to be adopted for eliminating the nitrogen. Upon a moderate scale and where there is a supply of alternating current, the method of oxidation, as in the analyses, is probably the more convenient. In this case it may be an advantage to retain the oxygen. If the oxygen content be about 60 per cent, as in the third experiment, the proportion is about sufficient to oxidize the nitrogen. We may compare this with the mixture of atmospheric air and oxygen which behaves in the same manner. In the latter case the proportion of argon would be reduced from 2.0 per cent to about 0.4 per cent, so that the advantage of using the liquid air amounts to about *five* times. In an arrangement that I have described for oxidizing nitrogen upon a large scale, the mixed gases were absorbed at the rate of 20 litres per hour.

In the alternative method the nitrogen is absorbed by magnesium or calcium. In this case it is necessary first to remove the oxygen; but oxygen is so much more easily dealt with than nitrogen that its presence, even in large proportion, is scarcely an objection. On this view and on the supposition that liquid air is available in large quantities, it is advantageous to allow the evaporation to proceed to great lengths. A 20 per cent mixture of argon and nitrogen (Experiment 5) is readily obtained.

Although the preparation of a considerable quantity of argon is rather an undertaking, there is no difficulty in demonstrating its existence with the most ordinary appliances. By the use of a specially shaped tube and an ordinary induction-coil actuated by a small Grove battery, I was able to show the characteristic spectrum of argon at atmospheric pressure, starting with 5 cc only of air.

Another question relating to the gases of the atmosphere has occupied my attention - namely the amount of free hydrogen. It may be remembered that M. A. Gautier, as the result of very elaborate investigations, announced that the amount of free hydrogen reached $2/10,000$, in addition to variable quantities of hydrocarbons dependent upon the locality where the air was collected. My own earlier observations related to the visibility of the C-line in sparks taken through carefully dried air at atmospheric pressure. This line could never be entirely eliminated, but with precaution could be made somewhat faint. When (country) air to which $1/5,000$ of hydrogen had been added was substituted for the pure air, the visibility of C was markedly increased; and the difference was such that one might easily believe that the proportion of hydrogen actually operative had been doubled. This conclusion would be in precise accordance with M. Gautier, could we assume that the smaller quantity of hydrogen really accompanied the air. But other observations rendered this assumption extremely doubtful.

In the first place the visibility of C with ordinary air was not perceptibly diminished by passage of the air over red-hot copper oxide. It may be argued that this reagent is not competent in moderate length to remove the last traces of hydrogen from air, even though the air be passed over it in a slow stream. I found, however, on a former occasion that hydrogen purposely introduced into nitrogen could be so far removed in this way that the density remained sensibly unaffected, although $1/10,000$ of residual hydrogen might be expected to manifest itself

Moreover, when air purposely contaminated as above with $1/5,000$ of hydrogen was passed over the copper oxide, the additional hydrogen appeared to be removed, the visibility of C reducing itself to that corresponding to untreated air.

Subsequently further spectroscopic experiments were made in which the platinum points were replaced by points of aluminium; and the evidence could hardly be reconciled with Gautier's view without coincidences of little *a priori* probability.

I was accordingly induced to make determinations by direct combustion. Ten litres of fresh *country* air dried as thoroughly as possible were passed over copper oxide at a red heat. The gain in weight of a phosphoric tube through which the air subsequently passed indicated an amount of free hydrogen corresponding to only about one-seventh of that recorded by Gautier, even though no allowance be made for the possible presence of hydrocarbons.

A defective gain of weight can hardly be explained as due to faulty manipulation. The important question is as to the efficiency of the copper oxide. Did my furnace tube allow the main part of the free hydrogen to pass unburnt? The question is one that can hardly be answered directly, but I may say that variations of temperature (within moderate limits) did not affect the result.

What it is possible to examine satisfactorily is the effect of small additions of hydrogen to the air as collected. In my later experiments the added hydrogen was only 1 cc, that is 1/10,000 by volume, or half the quantity originally present according to M. Gautier. The hydrogen was first diluted in a gas pipette with about 100 cc of air and allowed time to diffuse. The 10-litre aspirating-bottle being initially full of water, the diluted hydrogen was introduced at the top and was followed by 10 litres of air from the open, after which the mixture stood overnight, precautions which had been found sufficient to ensure a complete mixture in the spectroscopic work. The results showed an *additional* gain of 0.00072 grams, very nearly the full amount (0.00075) corresponding to the 1 cc of added hydrogen. We may say then that the copper oxide was competent to account for a small *addition* of hydrogen to air.

Another branch of my work upon gases has relation to the law of pressure, especially at low pressures. Under these circumstances the usual methods are deficient in accuracy. Thus Amagat considers that under the best conditions it is not possible to answer for anything less than 0.01 mm of mercury. By the use of a special manometer I was able to carry the accuracy at least 50 times further than Amagat's standard, and thus to investigate with fair accuracy the effect of pressures not exceeding 0.01 mm in total amount. Boyle's law was fully verified, even in the case of oxygen, for which C. Baur had found anomalies, especially in the neighbourhood of 0.7 mm pressure.

More recently I have made determinations of the compressibility of gases between one atmosphere and half an atmosphere of pressure. For this purpose two manometric gauges, each capable of measuring half an atmosphere, were employed. The equality of the gauges could be tested by using them *in parallel*, to borrow an electrical term. One of the gauges alone would thus serve for half an atmosphere, while the two combined *in series* gave the whole atmosphere. In combination with these gauges volumes in the ratio of 2 : 1 were needed. Here again the desired result was arrived at by the use of two equal volumes, either alone or in combination. Any question as to

the precise equality of the two volumes is eliminated in each set of observations by using the two single volumes alternately. The mean result then necessarily corresponds to the half of the total volume, except in so far as the capacities of the vessels may be altered by change of pressure.

The annexed Table 2 gives a summary of results for the various gases.

Table 2.

<i>Gas</i>	<i>B</i>	<i>Temperature</i>
O ₂	1.00038	11.2
H ₂	0.99974	10.7
N ₂	1.00015	14.9
CO	1.00026	13.8
Air	1.00023	11.4
CO ₂	1.00279	15.0
N ₂ O	1.00327	11.0

Here

$$B = \frac{pv \text{ at } \frac{1}{2} \text{ atmos.}}{pv \text{ at } 1 \text{ atmos.}}$$

the temperature being the same at both pressures and having the value recorded. That *B* should be less than unity in the case of hydrogen and exceed that value for the other gases, is what was to be expected from the known behaviour at higher pressures.

The principal interest of these results is perhaps to calculate corrections to ratios of densities, as found at atmospheric pressure, so as to infer what the ratios would be in a state of great rarefaction. It is only under this condition that Avogadro's law can be expected to apply accurately, as I pointed out in 1892 in connection with oxygen and hydrogen.

In the case of nitrogen and oxygen, the correction is not important, and the original comparison of densities* is sensibly unaffected. According to this method the atomic weight of nitrogen is 14.01, in opposition to the 14.05 found by Stas.

* Rayleigh and Ramsay, *Phil. Trans.*, (1895).