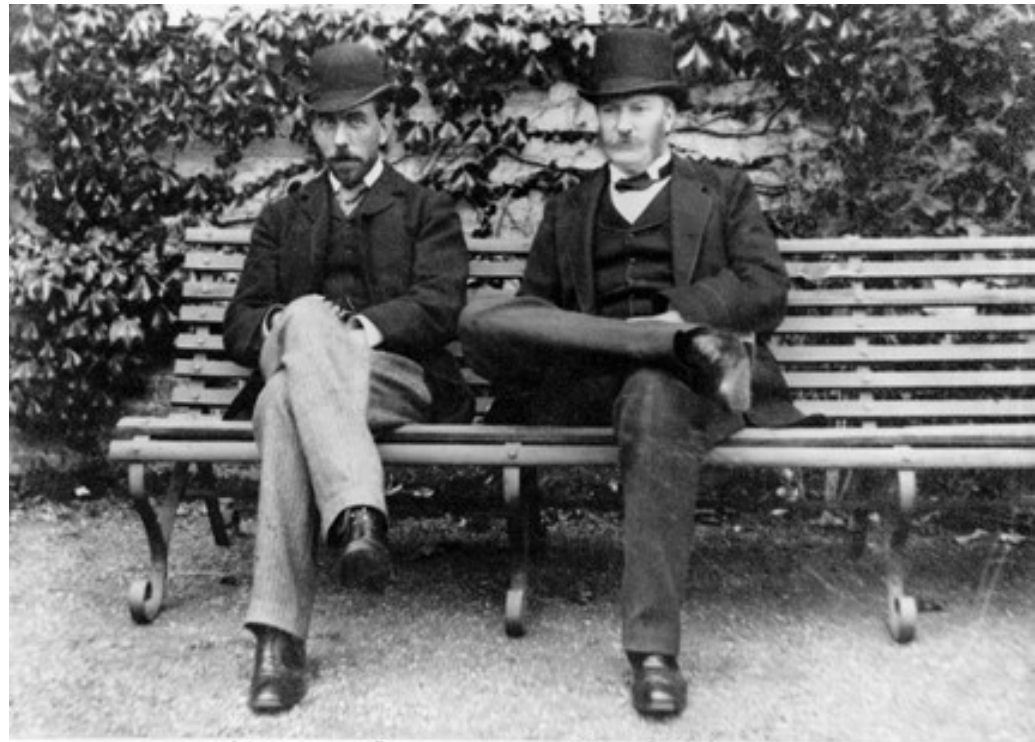


The Density of Gases in the Air and the Discovery of Argon

Rayleigh – Nobel Lecture (1904)



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Prof. William Ramsay. Rayleigh.
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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 the gas 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 atmospheric density.

It was assumed that the external volume of the working globe was the same whether vacuous or charged to atmospheric pressure. The introduction of the correction reduced Cooke's result to the same as that which I had in the mean time 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 sulfuric 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 finished. Afterwards, 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 density obtained by the two methods differed by a thousandth part – a difference small in itself but entirely beyond the experimental errors.

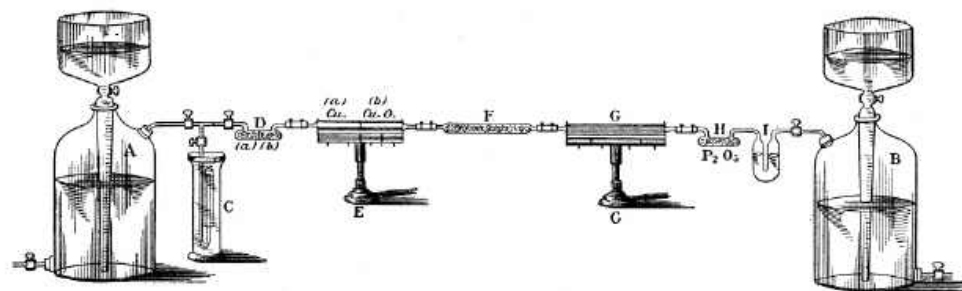


Fig. 1.

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 favored 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 niter 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.

$$C_p = C_v + R$$

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.

As regards the preparation of argon, it is advantageous to begin with liquid air, for preparation of which a plant is now to be found in many laboratories. 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.

