



On an Anomaly Encountered in Determinations of the Density of Nitrogen Gas

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April 19, 1894.

The LORD KELVIN, D.C.L., LL.D., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

Professor Dewar made an oral communication stating that he had observed that many bodies cooled to between -180° C. and -200° C. after stimulation by light become remarkably phosphorescent, not only in increased intensity, but in duration, and that liquid oxygen itself always shows faint but distinct phosphorescence. He stated that the details of experiments would be shortly communicated to the Society.

The following Papers were read :—

- I. "On an Anomaly encountered in Determinations of the Density of Nitrogen Gas." By LORD RAYLEIGH, Sec. R.S. Received February 16, 1894.

In a former communication* I have described how nitrogen, prepared by Lupton's method, proved to be lighter by about 1/1000 part than that derived from air in the usual manner. In both cases a red hot tube containing copper is employed, but with this difference. In the latter method the atmospheric oxygen is removed by oxidation of the copper itself, while in Lupton's method it combines with the hydrogen of ammonia, through which the air is caused to pass on its way to the furnace, the copper remaining unaltered. In order to exaggerate the effect, the air was subsequently replaced by oxygen. Under these conditions the whole, instead of only about one-seventh part of the nitrogen is derived from ammonia, and the discrepancy was found to be exalted to about one-half per cent.

Upon the assumption that similar gas should be obtained by both methods, we may explain the discrepancy by supposing either that the atmospheric nitrogen was too heavy on account of imperfect removal of oxygen, or that the ammonia nitrogen was too light on account of contamination with gases lighter than pure nitrogen. In-

* "On the Densities of the Principal Gases," 'Roy. Soc. Proc.,' vol. 53, p. 146, 893.

dependently of the fact that the action of the copper in the first case was pushed to great lengths, there are two arguments which appeared to exclude the supposition that oxygen was still present in the prepared gas. One of these depends upon the large quantity of oxygen that would be required in view of the small difference between the weights of the two gases. As much as $1/30$ th part of oxygen would be necessary to raise the density by $1/200$, or about one sixth of all the oxygen originally present. This seemed to be out of the question. But even if so high a degree of imperfection in the action of the copper could be admitted, the large alteration caused by the substitution of oxygen for air in Lupton's process would remain unexplained. Moreover, as has been described in the former paper, the introduction of hydrogen into the gas made no difference, such hydrogen being removed by the hot oxide of copper subsequently traversed. It is surely impossible that the supposed residual oxygen could have survived such treatment.

Another argument may be founded upon more recent results, presently to be given, from which it appears that almost exactly the same density is found when the oxygen of air is removed by hot iron reduced with hydrogen, instead of by copper, or in the cold by ferrous hydrate.

But the difficulties in the way of accepting the second alternative are hardly less formidable. For the question at once arises, of what gas, lighter than nitrogen, does the contamination consist? In order that the reader may the better judge, it may be well to specify more fully what were the arrangements adopted. The gas, whether air or oxygen, after passing through potash was charged with ammonia as it traversed a small wash-bottle, and thence proceeded to the furnace. The first passage through the furnace was in a tube packed with metallic copper, in the form of fine wire. Then followed a wash-bottle of sulphuric acid by which the greater part of the excess of ammonia would be arrested, and a second passage through the furnace in a tube containing copper oxide. The gas then traversed a long length of pumice charged with sulphuric acid, and a small wash-bottle containing Nessler solution. On the other side of the regulating tap the arrangements were always as formerly described, and included tubes of finely divided potash and of phosphoric anhydride. The rate of passage was usually about half a litre per hour.

Of the possible impurities, lighter than nitrogen, those most demanding consideration are hydrogen, ammonia, and water vapour. The last may be dismissed at once, and the absence of ammonia is almost equally certain. The question of hydrogen appears the most important. But this gas, and hydrocarbons, such as CH_4 , could they be present, should be burnt by the copper oxide; and the experiments already referred to, in which hydrogen was purposely introduced

into atmospheric nitrogen, seem to prove conclusively that the burning would really take place. Some further experiments of the same kind will presently be given.

The gas from ammonia and oxygen was sometimes odourless, but at other times smelt strongly of nitrous fumes, and, after mixture with moist air, reddened litmus paper. On one occasion the oxidation of the nitrogen went so far that the gas showed colour in the blow-off tube of the Töppler, although the thickness of the layer was only about half an inch. But the presence of nitric oxide is, of course, no explanation of the abnormal lightness. The conditions under which the oxidation takes place proved to be difficult of control, and it was thought desirable to examine nitrogen derived by *reduction* from nitric and nitrous oxides.

The former source was the first experimented upon. The gas was evolved from copper and diluted nitric acid in the usual way, and, after passing through potash, was reduced by *iron*, copper not being sufficiently active, at least without a very high temperature. The iron was prepared from blacksmith's scale. In order to get quit of carbon, it was first treated with a current of oxygen at a red heat, and afterwards reduced by hydrogen, the reduction being repeated after each employment. The greater part of the work of reducing the gas was performed outside the furnace, in a tube heated locally with a Bunsen flame. In the passage through the furnace in a tube containing similar iron the work would be completed, if necessary. Next followed washing with sulphuric acid (as required in the ammonia process), a second passage through the furnace over copper oxide, and further washing with sulphuric acid. In order to obtain an indication of any unreduced nitric oxide, a wash-bottle containing ferrous sulphate was introduced, after which followed the Nessler test and drying tubes, as already described. As thus arranged, the apparatus could be employed without alteration, whether the nitrogen to be collected was derived from air, from ammonia, from nitric oxide, from nitrous oxide, or from ammonium nitrite.

The numbers which follow are the weights of the gas contained by the globe at zero, at the pressure defined by the manometer when the temperature is 15°. They are corrected for the errors in the weights, but not for the shrinkage of the globe when exhausted, and thus correspond to the number 2·31026, as formerly given for nitrogen.

Nitrogen from NO by Hot Iron.

November 29, 1893	2·30143	}	Mean, 2·30008
December 2, 1893	2·29890		
December 5, 1893	2·29816		
December 6, 1893	2·30182		

Nitrogen from N₂O by Hot Iron.*

December 26, 1893.....	2.29869	} Mean, 2.29904
December 28, 1893.....	2.29940	

Nitrogen from Ammonium Nitrite passed over Hot Iron.

January 9, 1894.....	2.29849	} Mean, 2.29869
January 13, 1894.....	2.29889	

With these are to be compared the weights of nitrogen derived from the atmosphere.

Nitrogen from Air by Hot Iron.

December 12, 1893.....	2.31017	} Mean, 2.31003
December 14, 1893.....	2.30986 (H)	
December 19, 1893.....	2.31010 (H)	
December 22, 1893.....	2.31001	

Nitrogen from Air by Ferrous Hydrate.

January 27, 1894.....	2.31024	} Mean, 2.31020
January 30, 1894.....	2.31010	
February 1, 1894.....	2.31028	

In the last case a large volume of air was confined for several hours in a glass reservoir with a mixture of slaked lime and ferrous sulphate. The gas was displaced by deoxygenated water, and further purified by passage through a tube packed with a similar mixture. The hot tubes were not used.

If we bring together the means for atmospheric nitrogen obtained by various methods, the agreement is seen to be good, and may be regarded as inconsistent with the supposition of residual oxygen in quantity sufficient to influence the weights.

Atmospheric Nitrogen.

By hot copper, 1892.....	2.31026
By hot iron, 1893.....	2.31003
By ferrous hydrate, 1894.....	2.31020

Two of the results relating to hot iron, those of December 14 and December 19, were obtained from nitrogen, into which hydrogen had been purposely introduced. An electrolytic generator was inserted between the two tubes containing hot iron, as formerly described. The generator worked under its own electromotive force, and the current was measured by a tangent galvanometer. Thus, on December 19, the deflection throughout the time of filling was 3°, repre-

* The N₂O was prepared from zinc and very dilute nitric acid.

senting about 1/15 ampère. In two hours and a half the hydrogen introduced into the gas would be about 70 c.c., sufficient, if retained, to reduce the weight by about 4 per cent. The fact that there was no sensible reduction proves that the hydrogen was effectively removed by the copper oxide.

The nitrogen, obtained altogether in four ways from chemical compounds, is materially lighter than the above, the difference amounting to about 11 mg., or about 1/200 part of the whole. It is also to be observed that the agreement of individual results is less close in the case of chemical nitrogen than of atmospheric nitrogen.

I have made some experiments to try whether the densities were influenced by exposing the gas to the silent electric discharge. A Siemens tube, as used for generating ozone, was inserted in the path of the gas after desiccation with phosphoric anhydride. The following were the results :—

Nitrogen from Air by Hot Iron, Electrified.

January 1, 1894.	2·31163	}	Mean, 2·31059
January 4, 1894.	2·30956		

Nitrogen from N₂O by Hot Iron, Electrified.

January 2, 1894.	2·30074	}	Mean, 2·30064
January 5, 1894.	2·30054		

The somewhat anomalous result of January 1 is partly explained by the failure to obtain a subsequent weighing of the globe empty, and there is no indication that any effect was produced by the electrification.

One more observation I will bring forward in conclusion. Nitrogen prepared from oxygen and ammonia, and about one-half per cent. lighter than ordinary atmospheric nitrogen, was stored in the globe for eight months. The globe was then connected to the apparatus, and the pressure was re-adjusted in the usual manner to the standard conditions. On re-weighing no change was observed, so that the abnormally light nitrogen did not become dense by keeping.

II. "On Variations observed in the Spectra of Carbon Electrodes, and on the Influence of one Substance on the Spectrum of another." By W. N. HARTLEY, F.R.S., Royal College of Science, Dublin. Received January 13, 1894.

In a recently published paper by Eder and Valenta, on the "Line Spectrum of Elementary Carbon and the Ultra-violet Spark Spectrum of Wet and Dry Wood Charcoal" (Vienna, 'Akad. Wiss. Denkschriften,' vol. 60, 1893), there occurs this passage :—