

March 7, 1889.

Professor G. G. STOKES, D.C.L., President, in the Chair.

The Presents received were laid on the table, and thanks ordered for them.

In pursuance of the Statutes, the names of the Candidates for election into the Society were read from the Chair, as follows:—

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| Aitken, John. | Ewart, Professor J. Cossar, M.D. |
| Anderson, William, M.I.C.E. | Fleming, George, C.B. |
| Armstrong, Robert Young, Lieut-
Col., R.E. | Fletcher, Lazarus, M.A. |
| Ballard, Edward, M.D. | Frankland, Professor Percy Fara-
day, B.Sc. |
| Basset, Alfred Barnard, M.A. | Galloway, William. |
| Bosanquet, Robert Holford Mac-
dowall, M.A. | Gilchrist, Percy C. |
| Brown, Horace T., F.C.S. | Gordon, James Edward Henry,
B.A. |
| Burbury, Samuel Hawkesley, M.A. | Hammond, James, M.A. |
| Buzzard, Thomas, M.D. | Harcourt, Leveson Francis
Vernon, M.A. |
| Cameron, Sir Charles Alexander,
M.D. | Hemsley, William Botting, A.L.S. |
| Carnelley, Professor Thomas,
D.Sc. | Hinde, George Jennings, Ph.D. |
| Clark, Latimer, C.E. | Howorth, Henry Hoyle. |
| Conroy, Sir John, Bart., M.A. | Hudson, Charles Thomas, M.A. |
| Corfield, William Henry, M.D. | Hughes, Professor Thomas
McKenny, M.A. |
| Cunningham, Professor Daniel
John, M.D. | King, George. |
| Cunningham, Professor David
Douglas, M.B. | Lansdell, Rev. Henry, D.D. |
| Dawson, George Mercer, D.Sc. | Lydekker, Richard, B.A. |
| Dibdin, W. J., F.C.S. | MacMahon, Percy Alexander,
Major, R.E. |
| Dickinson, William Howship,
M.D. | Maitland, Major-General Eardley,
C.B. |
| Dreschfeld, Professor Julius,
F.R.C.P. | Martin, John Biddulph, M.A. |
| Dresser, Henry Eales, F.L.S. | Miall, Professor Louis C. |
| Eaton, Rev. Alfred Edwin, M.A. | Mond, Ludwig, F.C.S. |
| Elgar, Professor Francis, LL.D. | Ord, William Miller, M.D. |
| | Palmer, Henry Spencer, Major-
General, R.E. |

Pedler, Professor Alexander, F.C.S.	Stewart, J. H. M. Shaw, Major- Gen., R.E.
Poulton, Edward B., M.A.	Sutton, J. Bland, F.R.C.S.
Roberts, Isaac, F.R.A.S.	Thin, George, M.D.
Ross, James, M.D.	Thompson, Professor Silvanus Phillips, D.Sc.
Sankey, Matthew Henry P. R., Capt., R.E.	Thomson, Professor John Millar, F.R.S.E.
Saunders, Howard, F.L.S.	Tidy, Professor Charles Meymott, M.B.
Seebohm, Henry, F.L.S.	Todd, Charles, M.A.
Sharp, David, M.B.	Tomlinson, Herbert, B.A.
Shaw, William Napier, M.A.	Weldon, Walter Frank Raphael, M.A.
Smith, Willoughby.	Whitehead, Charles, F.L.S.
Sollas, Professor William John- son, D.Sc.	Yeo, Professor Gerald F., M.D.
Stebbing, Rev. Thomas Roscoe Rede, M.A.	
Stevenson, Thomas, M.D.	

The following Papers were read:—

I. "On the Composition of Water." By LORD RAYLEIGH,
Sec. R.S. Received February 26, 1889.

During the past year I have continued the work described in a former communication on the relative densities of hydrogen and oxygen,* in the hope of being able to prepare lighter hydrogen than was then found possible. To this end various modifications have been made in the generating apparatus. Hydrogen has been prepared from potash in place of acid. In one set of experiments the gas was liberated by aluminium. In this case the generator consisted of a large closed tube sealed to the remainder of the apparatus; and the aluminium was attached to an iron armature so arranged that by means of an external electro-magnet it was possible to lower it into the potash, or to remove it therefrom. The liberated gas passed through tubes containing liquid potash,† corrosive sublimate, finely powdered solid potash, and, lastly, a long length of phosphoric anhydride. But the result was disappointing; for the hydrogen proved to be no lighter than that formerly obtained from sulphuric acid.

I have also tried to purify hydrogen yet further by absorption in palladium. In his recent important memoir,‡ "On the Combustion of weighed Quantities of Hydrogen and the Atomic Weight of Oxygen,"

* 'Roy. Soc. Proc.,' February, 1888 (vol. 43, p. 356).

† Of course this tube was superfluous in the present case, but it was more convenient to retain it.

‡ 'Amer. Chem. Journ.,' vol. 10, No. 4.

Mr. Keiser describes experiments from which it appears that palladium will not occlude nitrogen—a very probable impurity in even the most carefully prepared gas. My palladium was placed in a tube sealed, as a lateral attachment, to the middle of that containing the phosphoric anhydride; so that the hydrogen was submitted in a thorough manner to this reagent both before and after absorption by the palladium. Any impurity that might be rejected by the palladium was washed out of the tube by a current of hydrogen before the gas was collected for weighing. But as the result of even this treatment I have no improvement to report, the density of the gas being almost exactly as before.

Hitherto the observations have related merely to the densities of hydrogen and oxygen, giving the ratio 15·884, as formerly explained. To infer the composition of water by weight, this number had to be combined with that found by Mr. Scott as representing the ratio of volumes. The result was

$$\frac{2 \times 15\cdot884}{1\cdot9965} = 15\cdot914.$$

The experiments now to be described are an attempt at an entirely independent determination of the relative weights by actual combustion of weighed quantities of the two gases. It will be remembered that in Dumas's investigation the composition of water is inferred from the weights of the oxygen and of the water, the hydrogen being unweighed. In order to avoid the very unfavourable conditions of this method, recent workers have made it a point to weigh the hydrogen, whether in the gaseous state as in the experiments of Professor Cooke and my own, or occluded in palladium as in Mr. Keiser's practice. So long as the hydrogen is weighed, it is not very material whether the second weighing relate to the water or to the oxygen. The former is the case in the work of Cooke and Keiser, the latter in the preliminary experiments now to be reported.

Nothing could be simpler in principle than the method adopted. Globes of the same size as those employed for the density determinations are filled to atmospheric pressure with the two gases, and are then carefully weighed. By means of Sprengel pumps the gases are exhausted into a mixing chamber, sealed below with mercury, and thence by means of a third Sprengel are conducted into a eudiometer, also sealed below with mercury, where they are fired by electric sparks in the usual way. After sufficient quantities of the gases have been withdrawn, the taps of the globes are turned, the leading tubes and mixing chamber are cleared of all remaining gas, and, after a final explosion in the eudiometer, the nature and amount of the residual gas are determined. The quantities taken from the globes can be found from the weights before and after operations.

From the quantity of that gas which proved to be in excess, the calculated weight of the residue is subtracted. This gives the weight of the two gases which actually took part in the combustion.

In practice, the operation is more difficult than might be supposed from the above description. The efficient capacity of the eudiometer being necessarily somewhat limited, the gases must be fed in throughout in very nearly the equivalent proportions; otherwise there would soon be such an accumulation of residue that no further progress could be made. For this reason nothing could be done until the intermediate mixing chamber was provided. In starting a combustion, this vessel, originally full of mercury, was charged with equivalent quantities of the two gases. The oxygen was first admitted until the level of the mercury had dropped to a certain mark, and subsequently the hydrogen down to a second mark, whose position relatively to the first was determined by preliminary measurements of volume. The mixed gases might then be drawn off into the eudiometer until exhausted, after which the chamber might be recharged as before. But a good deal of time may be saved by replenishing the chamber from the globes simultaneously with the exhaustion into the eudiometer. In order to do this without losing the proper proportion, simple mercury manometers were provided for indicating the pressures of the gases at any time remaining in the globes. But even with this assistance close attention was necessary to obviate an accumulation of residual gas in the eudiometer, such as would endanger the success of the experiment, or, at least, entail tedious delay. To obtain a reasonable control, two sparking places were provided, of which the upper was situate nearly at the top of the eudiometer. This was employed at the close, and whenever in the course of the combustion the residual gas chanced to be much reduced in quantity; but, as a rule, the explosions were made from the lower sparking point. The most convenient state of things was attained when the tube contained excess of oxygen down to a point somewhat below the lower sparking wires. Under these circumstances, each bubble of explosive gas readily found its way to the sparks, and there was no tendency to a dangerous accumulation of mixed gas before an explosion took place. When the gas in excess was hydrogen, the manipulation was more difficult, on account of the greater density of the explosive gas retarding its travel to the necessary height.

In spite of all precautions several attempted determinations have failed from various causes, such as fracture of the eudiometer and others which it is not necessary here to particularise, leading to the loss of much labour. Five results only can at present be reported, and are as follows:—

December 24, 1888.....	15·93
January 3, 1889.....	15·98
„ 21, „	15·98
February 2, „	15·93
„ 13, „	15·92
Mean.....	15·95

This number represents the atomic ratio of oxygen and hydrogen as deduced immediately from the weighings with allowance for the unburnt residue. It is subject to the correction for buoyancy rendered necessary by the shrinkage of the external volume of the globes when internally exhausted, as explained in my former communication.* In these experiments, the globe which contained the hydrogen was the same (14) as that employed for the density determinations. The necessary correction is thus four parts in a thousand, reducing the final number for the atomic weight of oxygen to

15·89,

somewhat lower than that which I formerly obtained (15·91) by the use of Mr. Scott's value of the volume ratio. It may be convenient to recall that the corresponding number obtained by Cooke and Richards (corrected for shrinkage) is 15·87, while that of Keiser is 15·95.

In the present incomplete state of the investigation, I do not wish to lay much stress upon the above number, more especially as the agreement of the several results is not so good as it should be. The principal source of error, of a non-chemical character, is in the estimation of the weight of the hydrogen. Although this part of the work cannot be conducted under quite such favourable conditions as in the case of a density determination, the error in the difference of the two weighings should not exceed 0·0002 gram. The whole weight of the hydrogen used is about 0·1 gram; † so that the error should not exceed three in the last figure of the final number. It is thus scarcely possible to explain the variations among the five numbers as due merely to errors of the weighings.

* The necessity of this correction was recognised at an early stage, and, if I remember rightly, was one of the reasons which led me to think that a redetermination of the density of hydrogen was desirable. In the meantime, however, the question was discussed by Agamennone ('Atti (Rendiconti) d. R. Accad. dei Lincei,' 1885), and some notice of his work reached me. When writing my paper last year I could not recall the circumstances; but since the matter has attracted attention I have made inquiry, and take this opportunity of pointing out that the credit of first publication is due to Agamennone.

† It was usual to take for combustion from two-thirds to three-fourths of the contents of the globe.

The following are the details of the determination of February 2, chosen at random :—

Before combustion . . . $G_{14} + H + 0.2906 = G_{11}$. . . pointer 20.05
 After ,, . . . $G_{14} + H + 0.4006 = G_{11}$. . . pointer 20.31

Hydrogen taken = $0.1100 - 0.00005 = 0.10995$ gram.

Before combustion . . . $G_{13} + O = G_{11} + 2.237$. . . pointer 20.00
 After ,, . . . $G_{13} + O = G_{11} + 1.357$. . . pointer 19.3

Oxygen taken = $0.8800 + 0.0001 = 0.8801$ gram.

At the close of operations the residue in the eudiometer was oxygen, occupying 7.8 c.c. This was at a total pressure of $29.6 - 16.2 = 13.4$ inches of mercury. Subtracting 0.4 inch for the pressure of the water vapour, we get 13.0 as representing the oxygen pressure. The temperature was about 12° C. Thus, taking the weight of a cub. cent. of oxygen at 0° C. and under a pressure of 76.0 cm. of mercury to be 0.00143 gram, we get as the weight of the residual oxygen

$$0.00143 \frac{7.8}{1 + 12 \times 0.00367} \frac{13.0 \times 2.54}{76.0} = 0.0046 \text{ gram.}$$

The weight of oxygen burnt was, therefore, $0.8801 - 0.0046 = 0.8755$ gram.

Finally, for the ratio of atomic weights,

$$\frac{\text{Oxygen}}{\frac{1}{2} \text{Hydrogen}} = 15.926.$$

In several cases the residual gas was subjected to analysis. Thus, after the determination of February 2, the volume was reduced by additions of hydrogen to 1.2 c.c. On introduction of potash there was shrinkage to about 0.9, and, on addition of pyrogallic acid, to 0.1 or 0.2. These volumes of gas are here measured at a pressure of $\frac{1}{3}$ atmosphere, and are, therefore, to be divided by 3 if we wish to estimate the quantities of gas under standard conditions. The final residue of (say) 0.05 c.c. should be nitrogen, and, even if originally mixed with the hydrogen—the most unfavourable case—would involve an error of only $\frac{1}{20000}$ in the final result. The 0.1 c.c. of carbonic anhydride, if originally contained in the hydrogen, would be more important; but this is very improbable. If originally mixed with the oxygen, or due to leakage through india-rubber into the combustion apparatus, it would lead to no appreciable error.

The aggregate impurity of 0.15, here indicated, is tolerably satisfactory in comparison with the total quantity of gas dealt with—

2000 c.c. It is possible, however, that nitrogen might be oxidised, and thus not manifest itself under the above tests. In another experiment the water of combustion was examined for acidity, but without definite indications of nitric acid. The slight reddening observed appeared to be rather that due to carbonic acid, some of which, it must be remembered, would be dissolved in the water. These and other matters demand further attention.

The somewhat complicated glass blowing required for the combustion apparatus has all been done at home by my assistant, Mr. Gordon, on whom has also fallen most of the rather tedious work connected with the evacuation of globes and other apparatus, and with the preparation of the gases.

II. "On the Wave-length of the Principal Line in the Spectrum of the Aurora." By WILLIAM HUGGINS, D.C.L., LL.D., F.R.S. Received February 19, 1889.

Notwithstanding the large number of determinations by different observers, since Ångström in 1867, of the wave-length of the principal (and frequently the only) line in the spectrum of the Aurora, this value has not yet been accepted as definitely fixed with the degree of accuracy which is required for a final inquiry into its chemical origin. The uncertainty within rather wide limits, which seems still to obtain, has arisen mainly from the circumstance that in nearly all cases the observations have been made with a small direct-vision spectroscope, and under conditions which do not admit of an accurate determination of the value sought for. About half the number of some twenty-four observers agree pretty well, but among the results given by the others the differences are very large in relation to the accuracy which is required, though they are not greater, perhaps, than was to be expected from the circumstances under which the observations were made.

I think it is very desirable, therefore, that I should put on record some observations of the spectrum of the Aurora which I made in the year 1874, but which up to the present time have remained unpublished. These observations were made with a powerful spectroscope, and under conditions which enabled me to determine the wave-length of the principal line within narrow limits of error. The spectroscope was made by Sir Howard Grubb on the automatic principle of his father, Mr. Thomas Grubb. It is furnished with two "Grubb" compound prisms; each has 5 square inches of base, and gives nearly twice the dispersion of a single prism of 60°, namely, about 9° 6' from A to H.

The object-glasses of the collimator and telescope are 1.25 inch in