

for it seems probable that such large tooth-rudiments may be traceable in later stages.

In this investigation, the few points of uncertainty as to the minute structure of some of the tissues will in all probability be settled satisfactorily.*

DESCRIPTION OF FIGURE. $\times 40$.

The arrow points towards the middle line of the mouth.

- M. Mouth.
- s, e.* Superficial epithelium of oral cavity.
- m.* Sub-epithelial tissues forming tooth-sac immediately outside enamel-cap.
- a.* Outer membrane of enamel-cap.
- b.* Middle membrane of enamel-cap.
- c.* Inner membrane of enamel-cap; the enamel cells. The dark layer just external to the enamel cells represents the stratum intermedium of Hannover.
- d.* The dentine, of which the inner part stains faintly and shows the delicate dentinal tubes.
- s.* Space caused by shrinkage between enamel cells and the outer part of the tooth rudiment.
- p.* Tooth papilla.
- o.* The odontoblasts forming the superficial layer of the papilla.

III. "On the Relative Densities of Hydrogen and Oxygen. Preliminary Notice." By Lord RAYLEIGH, Sec. R.S., Professor of Natural Philosophy in the Royal Institution. Received February 2, 1888.

The appearance of Professor Cooke's important memoir upon the atomic weights of hydrogen and oxygen† induces me to communicate to the Royal Society a notice of the results that I have obtained with respect to the relative *densities* of these gases. My motive for undertaking this investigation, planned in 1882,‡ was the same as that which animated Professor Cooke, namely, the desire to examine whether the relative atomic weights of the two bodies really deviated from the simple ratio 1 : 16, demanded by Prout's Law. For this purpose a knowledge of the densities is not of itself sufficient; but it appeared to me that the other factor involved, viz., the relative atomic *volumes* of the two gases, could be measured with great accuracy by eudiometric methods, and I was aware that Mr. Scott had in view a redetermination of this number, since in great part carried out.§ If both investigations are

* This appears to have been already the case.—Feb. 6, 1888.

† "The Relative Values of the Atomic Weights of Hydrogen and Oxygen," by J. P. Cooke and T. W. Richards, 'Amer. Acad. Proc.,' vol. 23, 1887.

‡ Address to Section A, British Association 'Report,' 1882.

§ "On the Composition of Water by Volume," by A. Scott, 'Roy. Soc. Proc.,' June 16, 1887 (vol. 42, p. 396).

conducted with gases under the normal atmospheric conditions as to temperature and pressure, any small departures from the laws of Boyle and Charles will be practically without influence upon the final number representing the ratio of atomic weights.

In weighing the gas the procedure of Regnault was adopted, the working globe being compensated by a similar closed globe of the same external volume, made of the same kind of glass, and of nearly the same weight. In this way the weighings are rendered independent of the atmospheric conditions, and only small weights are required. The weight of the globe used in the experiments here to be described was about 200 grams, and the contents were about 1800 c.c.

The balance is by Oertling, and readings with successive release-ments of the beam and pans, but without removal of the globes, usually agreed to $\frac{1}{10}$ th mgrm. Each recorded weighing is the mean of the results of several releasements.

The balance was situated in a cellar, where temperature was very constant, but at certain times the air currents, described by Professor Cooke, were very plainly noticeable. The beam left swinging over night would be found still in motion when the weighings were commenced on the following morning. At other times these currents were absent, and the beam would settle down to almost absolute rest. This difference of behaviour was found to depend upon the distribution of temperature at various levels in the room. A delicate thermopile with reflecting cones was arranged so that one cone pointed towards the ceiling and the other to the floor. When the galvanometer indicated that the ceiling was the warmer, the balance behaved well, and *vice versa*. The reason is of course that air is stable when the temperature increases upwards, and unstable when heat is communicated below. During the winter months the ground was usually warmer than the rest of the room, and air currents developed themselves in the weighing closet. During the summer the air cooled by contact with the ground remained as a layer below, and the balance was undisturbed.

The principal difference to be noted between my arrangements and those of Professor Cooke is that in my case no desiccators were used within the weighing closet. The general air of the room was prevented from getting too damp by means of a large blanket, occasionally removed and dried before a fire.*

In Regnault's experiments the globe was filled with gas to the atmospheric pressure (determined by an independent barometer), and the temperature was maintained at zero by a bath of ice. The use of ice is no doubt to be recommended in the case of the heavier gases; but it involves a cleaning of the globe, and therefore diminishes some-

* I can strongly recommend this method. In twenty-four hours the blanket will frequently absorb two pounds of moisture.

what the comparability of the weighings, vacuous and full, on which everything depends. Hydrogen is so light that, except perhaps in the mean of a long series, the error of weighing is likely to be more serious than the uncertainty of temperature. I have therefore contented myself with enclosing the body of the globe during the process of filling in a wooden box, into which passed the bulbs of two thermometers, reading to tenths of a degree centigrade. It seems probable that the mean of the readings represents the temperature of the gas to about $\frac{1}{10}$ th degree, or at any rate that the differences of temperature on various occasions and with various gases will be given to at least this degree of accuracy. Indeed the results obtained with oxygen exclude a greater uncertainty.

Under these conditions the alternate full and empty weighings can be effected with the minimum of interference with the surface of the globe. The stalk and tap were only touched with a glove, and the body of the globe was scarcely touched at all. To make the symmetry as complete as possible, the counterpoising globe was provided with a similar case, and was carried backwards and forwards between the balance room and the laboratory exactly as was necessary for the working globe.

In my earliest experiments (1885) hydrogen and oxygen were prepared simultaneously in a U-shaped voltameter containing dilute sulphuric acid. Since the same quantity of acid can be used indefinitely, I hoped in this way to eliminate all extraneous impurity, and to obtain hydrogen contaminated only by small quantities of oxygen, and *vice versa*. The final purification of the gases was to be effected by passing them through red-hot tubes, and subsequent desiccation with phosphoric anhydride. In a few trials I did not succeed in obtaining good hydrogen, a result which I was inclined to attribute to the inadequacy of a red heat to effect the combination of the small residue of oxygen.* Meeting this difficulty, I abandoned the method for a time, purposing to recur to it after I had obtained experience with the more usual methods of preparing the gases. In this part of the investigation my experience runs nearly parallel with that of Professor Cooke. The difficulty of getting quit of the dissolved air when, as in the ordinary preparation of hydrogen, the acid is fed in slowly at the time of working, induced me to design an apparatus whose action can be suspended by breaking an external electrical contact. It may be regarded as a Smee cell thoroughly enclosed. Two points of difference may be noted between this apparatus and that of Professor Cooke. In my manner of working it was necessary that the generator should

* From Professor Cooke's experience it appears not improbable that the impurity may have been sulphurous acid. Is it certain that in his combustions no hydrogen (towards the close largely diluted with nitrogen) escapes the action of the cupric oxide?

stand an internal vacuum. To guard more thoroughly against the penetration of external air, every cemented joint was completely covered with vaseline, and the vaseline again with water. Again, the zincs were in the form of solid sheets, closely surrounding the platinised plate on which the hydrogen was liberated, and standing in mercury. It was found far better to work these cells by their own electromotive force, without stimulation by an external battery. If the plates are close, and the contact wires thick, the evolution of gas may be made more rapid than is necessary, or indeed desirable.

Tubes, closed by drowned stopcocks, are provided, in order to allow the acid to be renewed without breaking joints; but one charge is sufficient for a set of experiments (three to five fillings), and during the whole of the time occupied (10 to 14 days) there is no access of atmospheric air. The removal of dissolved air (and other volatile impurity) proved, however, not to be so easy as had been expected, even when assisted by repeated exhaustions, with intermittent evolution of hydrogen; and the results often showed a progressive improvement in the hydrogen, even after a somewhat prolonged preliminary treatment. In subsequent experiments greater precautions will be taken.* Experience showed that good hydrogen could not thus be obtained from zinc and ordinary "pure" sulphuric acid, or phosphoric acid, without the aid of purifying agents. The best results so far have been from sulphuric and hydrochloric acid, when the gas is passed in succession over liquid potash, through powdered corrosive sublimate, and then through powdered caustic potash. All the joints of the purifying tubes are connected by fusion, and a tap separates the damp from the dry side of the apparatus. The latter includes a large and long tube charged with phosphoric anhydride, a cotton wool filter, a blow-off tube sealed with mercury until the filling is completed, besides the globe itself and the Töppler pump. A detailed description is postponed until the experiments are complete. It may be sufficient to mention that there is but one india-rubber connexion,—that between the globe and the rest of the apparatus, and that the leakage through this was usually measured by the Töppler before commencing a filling or an evacuation.

The object of giving a considerable capacity to the phosphoric tube was to provide against the danger of a too rapid passage of gas through the purifying tubes at the commencement of a filling. Suppose the gas to be blowing off, all the apparatus except the globe (and the Töppler) being at a pressure somewhat above the atmospheric. The tap between the damp and dry sides is then closed, and that into the globe is opened. The gas which now enters some-

* Spectrum analysis appears to be incapable of indicating the presence of comparatively large quantities of nitrogen.

what rapidly is thoroughly dry, having been in good contact with the phosphoric anhydride. In this way the pressure on the dry side is reduced to about 2 inches of mercury, but this residue is sufficient to allow the damp side of the apparatus to be exhausted to a still lower pressure before the tap between the two sides of the apparatus is reopened. When this is done, the first movement of the gas is retrograde; and there is no danger at any stage of imperfect purification. The generator is then re-started until the gas (after from two of five hours) begins to blow off again.

In closing the globe some precaution is required to secure that the pressure therein shall really be that measured by the barometer. The mercury seal is at some distance from, and at a lower level than, the rest of the apparatus. After removal of the mercury the flow of gas is continued for about one minute, and then the tap between the dry and damp sides is closed. From three to five minutes more were usually allowed for the complete establishment of equilibrium before the tap of the globe was turned off. Experiments on oxygen appeared to show that two minutes was sufficient. For measuring the atmospheric pressure *two* standard mercury barometers were employed.

The evacuations were effected by the Töppler to at least $\frac{1}{20000}$, so that the residual gas (at any rate after one filling with hydrogen) could be neglected.

I will now give some examples of actual results. Those in the following tables relate to gas prepared from *sulphuric* acid, with subsequent purification, as already described:—

Globe (14), empty.

Date.	Left.	Right.	Balance reading.
1887.			
Oct. 27—Nov. 5.....	$G_{14} + 0.394$	G_{11}	22.66
Nov. 7—Nov. 8.....	22.89
Nov. 9—Nov. 10.....	23.00
Nov. 11—Nov. 12.....	21.72

Globe (14), full.

Date.	Left.	Right.	Balance reading.	Barometer.	Temperature.
				in.	C.
1887.					
Nov. 5—7..	$G_{14} + 0.2400$	G_{11}	20.52	29.416	14.7°
Nov. 8—9..	$G_{14} + 0.2364$	G_{11}	19.77	29.830	12.3
Nov. 10—11..	$G_{14} + 0.2360$	G_{11}	19.18	22.807	11.2
Nov. 12—14..	$G_{14} + 0.2340$	G_{11}	19.51	30.135	10.3

The second column shows that globe (14) and certain platinum weights were suspended from the left end of the beam, and the third column that (in this series) only the counterpoising globe (11) was hung from the right end. The fourth column gives the mean balance reading in divisions of the scale, each of which (at the time of the above experiments) represented 0.000187 gram. The degree of agreement of these numbers in the first part of the table gives an idea of the errors due to the balance, and to uncertainties in the condition of the exteriors of the globes. A minute and unsystematic correction depending upon imperfect compensation of volumes (to the extent of about 2 c.c.) need not here be regarded.

The weight of the hydrogen at each filling is deduced, whenever possible, by comparison of the "full" reading with the mean of the immediately preceding and following "empty" readings. The difference, interpreted in grams, is taken provisionally as the weight of the gas. Thus for the filling of Nov. 5—

$$H = 0.154 - 2.25 \times 0.000187 = 0.15358.$$

The weights thus obtained depend of course upon the temperature and pressure at the time of filling. Reduced to correspond with a temperature of 12°, and to a barometric height of 30 inches (but without a minute correction for varying temperature of the mercury) they stand thus—

November 5.....	0.15811
" 8.....	0.15807
" 10.....	0.15798
" 12.....	0.15792
	0.15802
Mean.....	0.15802

The hydrogen obtained hitherto with similar apparatus and purifying tubes from hydrochloric acid is not quite so light, the mean of two accordant series being 0.15812.

The weighing of oxygen is of course a much easier operation than in the case of hydrogen. The gas was prepared from chlorate of potash, and from a mixture of the chlorates of potash and soda. The discrepancies between the individual weighings were no more than might fairly be attributed to thermometric and manometric errors. The result reduced so as to correspond in all respects with the numbers for hydrogen is 2.5186.*

But before these numbers can be compared with the object of obtaining the relative densities, a correction of some importance is required, which appears to have been overlooked by Professor Cooke,

* An examination of the weights revealed no error worth taking into account at present.

as it was by Regnault. The weight of the gas is *not* to be found by merely taking the difference of the full and empty weighings, unless indeed the weighings are conducted *in vacuo*. The external volume of the globe is larger when it is full than when it is empty, and the weight of the air corresponding to this difference of volume must be *added* to the apparent weight of the gas.

By filling the globe with carefully boiled water, it is not difficult to determine experimentally the expansion per atmosphere. In the case of globe (14) it appears that under normal atmospheric conditions the quantity to be added to the apparent weights of the hydrogen and oxygen is 0.00056 gram.

The actually observed alteration of volume (regard being had to the compressibility of water) agrees very nearly with an *à priori* estimate, founded upon the theory of thin spherical elastic shells and the known properties of glass. The proportional value of the required correction, in my case about $\frac{4}{1000}$ of the weight of the hydrogen, will be for spherical globes proportional to a/t , where a is the radius of the globe, and t the thickness of the shell, or to V/W , if V be the contents, and W the weight of the glass. This ratio is nearly the same for Professor Cooke's globe and for mine; but the much greater departure of his globe from the spherical form may increase the amount of the correction which ought to be introduced.

In the estimates now to be given, which must be regarded as provisional, the apparent weight of the hydrogen is taken at 0.15804, so that the real weight is 0.15860. The weight of the same volume of oxygen under the same conditions is $2.5186 + 0.0006 = 2.5192$. The ratio of these numbers is 15.884.

The ratio of densities found by Regnault was 15.964, but the greater part of the difference may well be accounted for by the omission of the correction just now considered.

In order to interpret our result as a ratio of atomic weights, we need to know accurately the ratio of atomic volumes. The number given as most probable by Mr. Scott in May, 1887,* was 1.994, but he informs me that more recent experiments under improved conditions give 1.9965. Combining this with the ratio of densities, we obtain as the ratio of atomic weights—

$$\frac{2 \times 15.884}{1.9965} = 15.912.$$

It is not improbable that experiments conducted on the same lines, but with still greater precautions, may raise the final number by one or even two thousandths of its value.

The ratio obtained by Professor Cooke is 15.953; but the difference

* *Loc. cit.*

between this number and that above obtained may be more than accounted for, if I am right in my suggestion that his gas weighings require correction for the diminished buoyancy of the globe when the internal pressure is removed.

Presents, February 9, 1888.

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