

The *cardiac accelerator fibres* arise in the cat from the first four or five thoracic nerves; the maximum effect is obtained sometimes from the 2nd and sometimes from the 3rd thoracic nerve; the 1st and the 4th thoracic nerves have in some animals a considerable accelerator action, in others little or none; the 5th nerve appears occasionally to contain a few accelerator fibres, but further evidence is desirable.

Taking into account the pilo-motor fibres of the cat and dog, it is seen that the cervical sympathetic arises in these animals from the first seven, and in the rabbit from the first eight, thoracic nerves; the 1st thoracic is, however, less represented in the cervical sympathetic of the rabbit than it is in that of the cat and dog.

Comparing the rabbit with the cat and dog, as regards sympathetic fibres, which are present in all, it results that in the cat and dog the fibres of any one kind are higher in origin, and in some cases present in fewer spinal nerves, than they are in the rabbit. In accordance with this, the 2nd thoracic more frequently causes a movement of the fore-foot in the rabbit than in the other two animals. On the whole, the sympathetic fibres of any one kind appear to be slightly higher in the dog than in the cat.

The uppermost white ramus communicans arises from the 1st thoracic nerve; the lowest in the dog and cat arises usually, as described by Gaskell, from the 4th lumbar nerve; occasionally, however, the 5th lumbar nerve gives off a white ramus to the sympathetic. Both in the upper and lower regions of the spinal cord, there is satisfactory experimental evidence of efferent sympathetic fibres in those spinal nerves which have white rami, and in those only. This is in agreement with the views of Gaskell.

In the grey rami, medullated fibres of greater diameter than  $4\ \mu$ —and, perhaps, some of the smaller ones—are probably afferent fibres, which pass to the spinal cord by the white rami.

A comparison of the histological characters and of the reflex effects yielded by various parts of the sympathetic, by the depressor, and by the nervus erigens, affords strong evidence that a considerable number of the medullated fibres of larger diameter than  $4\ \mu$ , although afferent, are not fibres of general sensibility.

In the course of the paper the results of previous observers are given and discussed.

### III. "On the Relative Densities of Hydrogen and Oxygen. II."

By LORD RAYLEIGH, Sec. R.S. Received February 5, 1892.

In a preliminary notice upon this subject,\* I explained the procedure by which I found as the ratio of densities 15 884. The

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

hydrogen was prepared from zinc and sulphuric, or from zinc and hydrochloric, acid, and was liberated upon a platinum plate, the generator being in fact a Smee cell, enclosed in a vessel capable of sustaining a vacuum, and set in action by closing the electric circuit at an external contact. The hydrogen thus prepared was purified by corrosive sublimate and potash, and desiccated by passage through a long tube packed with phosphoric anhydride. The oxygen was from chlorate of potash, or from mixed chlorates of potash and soda.

In a subsequent paper on the Composition of Water,\* I attacked the problem by a direct synthesis of water from weighed quantities of the two component gases. The ratio of atomic weights thus obtained was 15·89.

At the time when these researches were commenced, the latest work bearing upon the subject dated from 1845, and the number then accepted was 15·96. There was, however, nothing to show that the true ratio really deviated from the 16:1 of Prout's law, and the main object of my work was to ascertain whether or not such deviation existed. About the year 1888, however, a revival of interest in this question manifested itself, especially in the United States, and several results of importance have been published. Thus, Professor Cooke and Mr. T. W. Richards found a number which, when corrected for an error of weighing that had at first been overlooked, became 15·869.

The substantial agreement of this number with those obtained by myself seemed at first to settle the question, but almost immediately afterwards there appeared an account of a research by Mr. Keiser, who used a method presenting some excellent features, and whose result was as high as 15·949. The discrepancy has not been fully explained, but subsequent numbers agree more nearly with the lower value. Thus, Noyes obtains 15·896, and Dittmar and Henderson give 15·866.

I had intended further to elaborate and extend my observations on the synthesis of water from weighed quantities of oxygen and hydrogen, but the publication of Professor E. W. Morley's masterly researches upon the "Volumetric Composition of Water"† led me to the conclusion that the best contribution that I could now make to the subject would be by the further determination of the relative densities of the two gases. The combination of this with the number 2·0002,‡ obtained by Morley as the mean of astonishingly concordant

\* 'Roy. Soc. Proc.,' vol. 45, p. 425, February, 1889.

† 'Amer. Journ. Sci.,' March, 1891.

‡ It should not be overlooked that this number is difficult to reconcile with views generally held as to the applicability of Avogadro's law to very rare gases. From what we know of the behaviour of oxygen and hydrogen gases under compression, it seems improbable that volumes which are as 2·0002 : 1 under atmo-

individual experiments, would give a better result for the atomic weights than any I could hope to obtain directly.

In all work of this sort, the errors to be contended with may be classed as either systematic or casual. The latter are eliminated by repetition, and are usually of no importance in the final mean. It is systematic errors that are most to be dreaded. But although directly of but little account, casual errors greatly embarrass a research by rendering difficult and tedious the detection of systematic errors. Thus, in the present case, almost the only source of error that can prejudice the final result is impurity in the gases, especially in the hydrogen. The better the hydrogen, the lighter it will prove; but the discrimination is blunted by the inevitable errors of weighing. After perhaps a week's work it may become clear that the hydrogen is a little at fault, as happened in one case from penetration of nitrogen between the sealed-in platinum electrodes and the glass of the generator.

Another difficulty, which affects the presentation of results, turns upon the one-sided character of the errors most to be feared. As has been said, impure hydrogen can only be too heavy, and another important source of error, depending upon imperfect establishment of equilibrium of pressure between the contents of the globe and the external atmosphere, also works one-sidedly in the same direction. The latter source of error is most to be feared immediately after a re-greasing of the tap of the globe. The superfluous grease finds its way into the perforation of the plug, and partially blocks the passage, so that the six minutes usually allowed for the escape of the initial excess of pressure in the globe may become inadequate. Partly from this cause and partly from incomplete washing out of nitrogen from the generator, the first filling of a set was so often found abnormally heavy that it became a rule in all cases to reject it. From these and other causes, such as accidental leakages not discovered at the time, it was difficult to secure a set of determinations in which the mean really represented the most probable value. At the same time, any arbitrary rejection of individual results must be avoided as far as possible.

In the present work two objects have been especially kept in view. The first is simplicity upon the chemical side, and the second the use of materials in such a form that the elimination of impurities goes forward in the normal working of the process. When, as in the former determinations, the hydrogen is made from zinc, any impurity which that material may contain and communicate to the gas cannot be eliminated from the generator; for each experiment spheric conditions would remain as 2 : 1 upon indefinite expansion. According to the formula of Van der Waals, a greater change than this in the ratio of volumes is to be expected.

brings into play a fresh quantity of zinc, with its accompanying contamination. Moreover, the supply of acid that can be included in one charge of the generator is inadequate, and good results are only obtained as the charge is becoming exhausted. These difficulties are avoided when zinc is discarded. The only material consumed during the experiments is then the water, of which a large quantity can be included from the first. On the other hand, the hydrogen liberated is necessarily contaminated with oxygen, and this must be removed by copper contained in a red-hot tube. In the experiments to be described the generator was charged with potash,\* and the gases were liberated at platinum electrodes. In the case of a hydrogen filling the oxygen blew off on one side from a mercury seal, and on the other the hydrogen was conveyed through hot tubes containing copper. The bulk of the aqueous vapour was deposited in a small flask containing strong solution of potash, and the gas then passed over solid potash to a long tube packed with phosphoric anhydride. Of this only a very short length showed signs of being affected at the close of all operations.

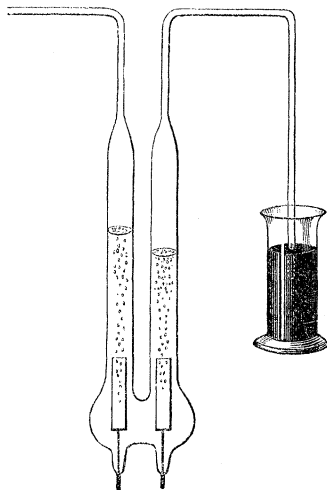
With respect to impurities, other than oxygen and oxides of hydrogen, which may contaminate the gas, we have the following alternative. Either the impurity is evolved much more rapidly than in proportion to the consumption of water in the generator, or it is not. If the rate of evolution of the impurity, reckoned as a fraction of the quantity originally present, is not much more rapid than the correspondingly reckoned consumption of water, the presence of the impurity will be of little importance. If on the other hand, as is probable, the rate of evolution is much more rapid than the consumption of water, the impurity is soon eliminated from the residue, and the gas subsequently generated becomes practically pure. A similar argument holds good if the source of the impurity be in the copper, or even in the phosphoric anhydride; and it applies with increased force when at the close of one set of operations the generator is replenished by the mere addition of water. It is, however, here assumed that the apparatus itself is perfectly tight.

Except for the reversal of the electric current, the action of the apparatus is almost the same whether oxygen or hydrogen is to be collected. In the latter case the copper in the hot tubes is in the reduced, and in the former case in the oxidised, state. For the sake of distinctness we will suppose that the globe is to be filled with hydrogen.

The generator itself (fig. 1) is of the U-form, with unusually long branches, and it is supplied from Grove cells with about 3 ampères of electric current. Since on one side the oxygen blows off into the

\* At the suggestion of Professor Morley, the solution was freed from carbonate, or nearly so, by the use of baryta, of which it contained a slight excess.

FIG. 1.



air, the pressure in the generator is always nearly atmospheric. Some trouble has been caused by leakage between the platinum electrodes and the glass. In the later experiments to be here recorded these joints were drowned with mercury. On leaving the generator the hydrogen traverses a red-hot tube of hard glass charged with copper,\* then a flask containing a strong solution of potash, and afterwards a second similar hot tube. The additional tube was introduced with the idea that the action of the hot copper in promoting the union of the hydrogen with its oxygen contamination might be more complete after removal of the greater part of the oxygen, whether in the combined or in the uncombined state. From this point onward the gas was nearly dry. In the earlier experiments the junctions of the hard furnace tubes with the soft glass of the remainder of the apparatus were effected by fusion. One of these joints remained in use, but the others were replaced by india-rubber connexions *drowned in mercury*. It is believed that no leakage occurred at these joints; but as an additional security a tap was provided between the generator and the furnace, and was kept closed whenever there was no forward current of hydrogen. In this way the liquid in the generator would be protected from any possible infiltration of nitrogen. Any that might find its way into the furnace tubes could easily be removed before the commencement of a filling.

Almost immediately upon leaving the furnace tubes the gas arrives

\* The copper must be free from sulphur; otherwise the contamination with sulphuretted hydrogen is somewhat persistent.

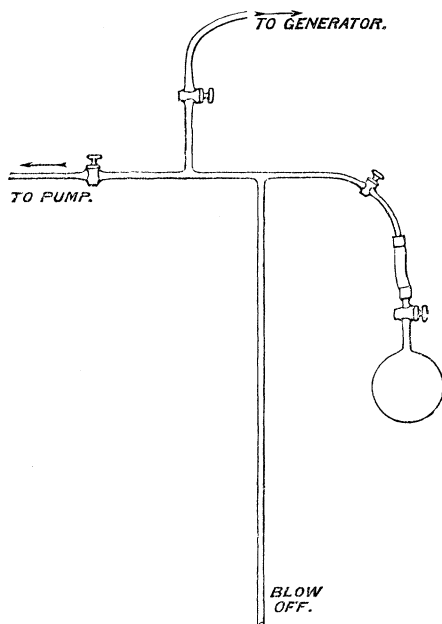
at a tap which for distinctness may be called the regulator. In the generator and in the furnace tubes the pressure must be nearly atmospheric, but in the globe there is (at the commencement) a vacuum. The transition from the one pressure to the other takes place at the regulator, which must be so adjusted that the flow through it is approximately equal to the production of gas. At first the manipulation of the regulator was a source of trouble and required almost constant attention, but a very simple addition gave the desired control. This was merely a long wooden arm, attached to the plug, which served both as a lever and as an indicator. Underneath the pointed extremity was a small table to which its motions could be referred. During the first two-thirds of a filling very little readjustment was needed, and the apparatus could be left for half an hour with but little fear of displacing too much the liquid in the generator. Towards the close, as the motive force fell off, the tap required to be opened more widely. Sometimes the recovery of level could be more conveniently effected by insertion of resistance into the electric circuit, or by interrupting it altogether for a few minutes. Into details of this kind it is hardly necessary to go further.

From the regulator the gas passed to the desiccating tubes. The first of these was charged with fragments of solid potash, and the second with a long length of phosphoric anhydride. Finally, a tube stuffed with glass wool intercepted any suspended matter that might have been carried forward.

The connexion of the globe with the generator, with the Töppler, and with the blow-off, is shown in the accompanying fig. 2. On the morning of a projected filling the vacuous globe would be connected with the free end of the stout-walled india-rubber tube, and secured by binding wire. The generator being cut off, a high vacuum would be made up to the tap of the globe. After a couple of hours' standing the leakage through the india-rubber and at the joints could be measured. The amount of the leakage found in the first two hours was usually negligible, considered as an addition to a globeful of hydrogen, and the leakage that would occur in the hours following would (in the absence of accidents) be still smaller. If the test were satisfactory, the filling would proceed as follows:—

The electric current through the generator being established and the furnace being heated, any oxygen that might have percolated into the drying tubes had first to be washed out. In order to do this more effectively, a moderate vacuum (of pressure equal to about 1 inch of mercury) was maintained in the tubes and up to the regulator by the action of the pump. In this way the current of gas is made very rapid, and the half hour allowed must have been more than sufficient for the purpose. The generator was then temporarily cut off, and a high vacuum produced in the globe connexion and in the blow-off

FIG. 2.



tube, which, being out of the main current of gas, might be supposed to harbour impurities. After this the pump would be cut off, the connexion with the generator re-established, and, finally, the tap of the globe cautiously opened.

The operation of filling usually occupied from two to three hours. When the gas began to blow off under an excess of pressure represented by about half an inch of mercury, the blow-off cistern was lowered so as to leave the extremity of the tube free. For two minutes the current of gas from the generator was allowed to flow through, after which the generator was cut off, and the globe left in simple communication with the atmosphere, until it was supposed that equilibrium of pressure had been sufficiently established. Doubts have at various times been felt as to the interval required for this purpose. If too little time is allowed, there will remain an excess of pressure in the globe, and the calculated weight of the filling will come out too high. On the other hand, an undue prolongation of the time might lead to a diffusion of air back into the globe. In a special experiment no abnormal weight was detected after half an hour's communication, so that the danger on this side appeared to be small. When the passages through the taps were free from grease, one or

two minutes sufficed for the establishment of equilibrium, but there was always a possibility of a partial obstruction. In the results to be presently given four minutes were allowed after the separation from the generator. It may be remarked that a part of any minute error that may arise from this source will be eliminated in the comparison with oxygen, which was collected under like conditions.

The reading of the barometers and thermometers at the moment when the tap of the globe was turned off took place as described in the former paper. The arrangements for the weighings were also the same.

In the evacuations the process was always continued until, as tested by the gauge of the Töppler after at least a quarter of an hour's standing, the residue could be neglected. Here, again, any minute error would be eliminated in the comparison of the two gases.

In the case of oxygen, the errors due to contamination (even with hydrogen) are very much diminished, and similar errors of weighing tell very much less upon the proportional agreement of the final numbers. A comparison of the actual results with the two kinds of gas does not, however, show so great an advantage on the side of the oxygen as might have been expected. The inference appears to be that the individual results are somewhat largely affected by temperature errors. Two thermometers were, indeed, used (on opposite sides) within the wooden box by which the globe is surrounded, and they could easily be read to within  $\frac{1}{10}^{\circ}$  C. But in other respects, the circumstances were unfavourable in consequence of the presence in the same room of the furnace necessary to heat the copper. An error of  $\pm 0.1^{\circ}$  C. in the temperature leads to a discrepancy of 1 part in 1500 in the final numbers. Some further elaboration of the screening arrangements actually employed would have been an improvement, but inasmuch as the circumstances were precisely the same for the two gases, no systematic error can here arise. The thermometers were, of course, the same in the two cases.

The experiments are grouped in five sets, two for oxygen and three for hydrogen. In each set the work was usually continued until the tap of the globe required re-greasing, or until, owing to a breakage or to some other accident, operations had to be suspended.



## Oxygen.

1891.	Weight.	Bar. temp., F.	Globe temp., C.
	grams.		
June 29 .....	2·5182	70	20°·85
July 2 .....	2·5173	69	20°·60
July 4 .....	2·5172	67½	19°·75
July 6 .....	2·5193	70½	21°·40
July 9 .....	2·5174	64	17°·60
July 10 .....	2·5177	65½	19°·05
Mean .....	2·51785	68	20°

The six fillings were all independent, except that of July 6, when the bulk of the oxygen remaining from the previous filling was not removed. It so happens that this case shows the greatest discrepancy, but there seems to be no sufficient reason for rejecting it.

## Hydrogen.

1891.	Weight.	Bar. temp., F.	Globe temp., C.
	gram.		
July 31 .....	0·15807	60½	15°·90
August 4 .....	0·15816	65	18°·00
August 6 .....	0·15811	66½	19°·20
August 8 .....	0·15803	65	18°·15
August 11 .....	0·15801	66	19°·15
August 13 .....	0·15809	68½	20°·10
Mean .....	0·15808	65	18°

## Hydrogen.

1891.	Weight.	Bar. temp., F.	Globe temp., C.
	gram		
September 22 .....	0·15800	58	14°·5
September 24 .....	0·15820	61½	16°·3
September 28 .....	0·15792	62	17°·6
September 30 .....	0·15788	63½	18°·1
October 2 .....	0·15783	62	17°·3
Mean .....	0·15797	61	17°

## Hydrogen.

1891.	Weight.	Bar. temp., F.	Globe temp., C.
	gram.		
October 26 .....	0·15807	55°	13°·30
October 28 .....	0·15801	56	14·00
October 31 .....	0·15817	50	10·95
November 3 .....	0·15790	53½	12·10
November 5 .....	0·15810	55	12·00
November 7 .....	0·15798	50	10·70
November 10 .....	0·15802	48	9·30
November 13 .....	0·15807	55½	12·70
Mean .....	0·15804	53	12°

## Oxygen.

1891.	Weight.	Bar. temp., F.	Globe temp., C.
	grams.		
November 31 .....	2·5183	53°	12°·15
December 3 .....	2·5168	56	13·55
December 5 .....	2·5172	56½	14·15
December 7 .....	2·5181	58½	14·70
December 8 .....	2·5156	51	11·15
Mean .....	2·5172	55	13°

In almost every case the weight of the globe *full* is compared with the mean of the immediately preceding and following weights *empty*. The numbers recorded in the second column are derived from the readings of the balance by the introduction of corrections—

(1.) For the errors of the weights themselves, found by a systematic comparison, only relative values uncorrected for buoyancy being required.

(2.) For the deviation of the mean\* barometric reading at the time of filling from 30 inches (as read upon the vernier).

(3.) For the deviation of the temperature of the barometers (Column 3) from 60° F.

(4.) For the deviation of the temperature of the gas (as read upon the thermometers) from 12° C.

As an example, I will take in detail the calculation for the hydrogen filling of October 26. After the evacuation of October 24, the working globe (14) with its compensating volume piece and

\* There were two barometers.

0.4778 gram stood on the left of the balance with globe (11) on the right. The position of equilibrium of the pointer, as determined after four different releasements, each observed in the usual manner, was 19.02 scale divisions. In like manner, after the evacuation of October 27, with the same weights in use, the equilibrium position of the pointer was 18.46. After the filling of October 26, the weights associated with (14) were 0.3220 gram, instead of 0.4778; and the pointer reading was 20.08. So far as the weights are concerned, the value of the hydrogen would be  $0.4778 - 0.3220$ , or 0.1558 gram; but to this we must add a correction corresponding to 1.34 scale divisions, being the difference between 20.08 and  $\frac{1}{2}(19.02 + 18.46)$ . At the time in question, the value of a scale division was 0.00020 gram, so that we obtain—

$$0.1558 + 0.00027 = 0.15607.$$

The particular weights in use on this occasion were such that no correction is necessary in order to allow for their errors.

The mean barometer reading at the time of filling was 29.742, so that the factor required on this account is 30 : 29.742. The correction for temperature of gas is from 13.3 to 12°.

$$\begin{array}{r} \text{Log } 0.15607 \dots\dots\dots = \bar{1}.19332 \\ \text{For barometer} \dots\dots\dots 0.00375 \\ \text{For temperature} \dots\dots\dots 0.00198 \\ \hline \text{Log } 0.15814 \dots\dots\dots = \bar{1}.19905 \end{array}$$

To this a correction for the temperature of the *barometer* has still to be applied. For 1° F. the correcting factor is (1 - 0.000089), or for 5° F. (1 - 0.000445). From 0.15814 we are thus to subtract 0.00007, giving the tabular number 0.15807.

A further minute correction to the mean of each set may be made for the temperature of the glass. A warm globe is larger than a cold one, and consequently holds more gas. If we suppose that the volume expansion of the glass per degree C. is 0.000025, we find, corrected to 12° C.—

#### Hydrogen.

1891.	Weight.	Bar. temp., F.	Globe temp., C.	Corrected to 12°.
	gram.			gram.
July.....	0.15808	65	18	0.158056
September .....	0.15797	61	17	0.157950
October .....	0.15804	53	12	0.158040
Mean .....		60	16	0.158015

## Oxygen.

1891.	Weight.	Bar. temp., F.	Globe temp., C.	Corrected to 12°.
	grams.	°	°	grams.
June .....	2·51785	68	20	2·51735
November .....	2·51720	55	13	2·51713
Mean .....		61½	16½	2·51724

The means here exhibited give the weights of the two gases as they would be found with the globe at 12° C., and the barometers at 60° F. and at 30 inches. The close agreement of the mean temperatures for the two gases shows how little room there is for systematic error dependent upon imperfections in the barometers and thermometers. But the results still require modification before they can be compared with the view of deducing the relative densities of the gases.

In the first place, there is a systematic, though minute, difference in the pressures hitherto considered as corresponding. The terminal of the blow-off tube is 33 inches below the centre of the globe at the time of filling. In the one case this is occupied by hydrogen, and in the other by oxygen. If we treat the latter as the standard, we must regard the hydrogen fillings as taking place under an excess of pressure equal to  $\frac{1}{16}$  of the weight of a column of oxygen 33 inches high; and this must be compared with 30 inches of mercury. Hence, if we take the sp. gr. of oxygen under atmospheric conditions at 0·0014, and that of mercury at 13·6, the excess of pressure under which the hydrogen was collected is as a fraction of the whole pressure

$$\frac{33}{30} \cdot \frac{15}{16} \cdot \frac{0\cdot0014}{13\cdot6} = 0\cdot000106;$$

and  $0\cdot000106 \times 0\cdot158 = 0\cdot000017$ . This, then, is what we must subtract from the weight of the hydrogen on account of the difference of pressures due to the gas in the blow-off tube. Thus

$$H = 0\cdot157998, \quad O = 2\cdot51724.$$

[These numbers are not quite comparable with those given in the former communication, inasmuch as the standard temperature then used for the barometers was 55° F. Reduced so as to correspond to 60°, the former numbers become

$$H = 0\cdot15797, \quad O = 2\cdot5174.$$

The agreement is satisfactory, especially when it is remembered that both gases were prepared by different methods in the two sets of experiments.—Feb. 17.]

But there is still another and a more important correction to be introduced. In my former paper it was shown that when the weighings are conducted in air the true weight of the gas contained in the globe is not given by merely subtracting the weight of the globe when empty from the weight when full. When the globe is empty, its external volume is less than when full, and thus, in order to obtain the true weight, the apparent weight of the gas must be increased by the weight of air whose volume is equal to the change of volume of the globe.

In order to determine the amount of this change of volume, the globe is filled to the neck with recently boiled distilled water, and the effect is observed upon the level in the stem due to a suction of, say, 20 inches of mercury. It is not advisable to carry the exhaustion much further for fear of approaching too nearly the point at which bubbles of vapour may be formed internally. In the earlier experiments, described in the preliminary note, the upper surface of the liquid was in the stem of the globe itself (below the tap), and the only difficulty lay in the accurate estimation of a change of volume occurring in a wide and somewhat irregular tube. The method employed was to produce, by introduction of a weighed quantity of mercury, a rise of level equal to that caused by the suction.

The advantage of this procedure lay in the avoidance of joints and of the tap itself, but, for the reasons given, the readings were not quite so accurate as might be desired. I wished, therefore, to supplement, if possible, the former determination by one in which the change of volume occurred in a tube narrower and of better shape. With this object in view, the stem of the globe was prolonged by a graduated tubular pipette attached with the aid of india-rubber. The tubes themselves were treated with gutta-percha cement, and brought almost into contact. It had hardly been expected that the joint would prove unyielding under the applied suction, but it was considered that the amount of the yielding could be estimated and allowed for by operations conducted *with tap closed*. The event, however, proved that the yielding at the joint was scarcely, if at all, perceptible.

The pipette, of bore such that 16 cm. corresponded to 1 c.c., was graduated to 0.01, and was read by estimation to 0.001 c.c. In order the better to eliminate the changes due to temperature, readings under atmospheric pressure, and under a suction of 20 inches of mercury, were alternated. On January 28, 1892, a first set gave 0.648 — 0.300 = 0.348, a second gave 0.6645 — 0.316 = 0.3485 and a third gave

$0.675 - 0.326 = 0.349$ . Similar operations with tap closed\* gave no visible movement.

The result of the day's experiments was thus 0.3485 for 20 inches, or 0.523 for 30 inches, suction. Similar experiments on January 28, at a different part of the graduation, gave 0.526. On this day the yielding with tap closed was just visible, and was estimated at 0.001. As a mean result, we may adopt 0.524 c.c. The graduation of the pipette was subsequently verified by weighing a thread of mercury that occupied a measured length.

A part of the above-measured volume is due to the expansion of the water when the pressure is relieved. We may take this at 0.000047 of the volume per atmosphere. The volume itself may be derived with sufficient accuracy for the present purpose from the weight of its oxygen contents. It is  $2.517/0.00137$ , or 1837 c.c. The expansion of the water per atmosphere is thus  $0.000047 \times 1837$ , or 0.087 c.c. This is to be subtracted from 0.524, and leaves 0.437 c.c. This number applies strictly to the volume enclosed within the glass, but the change in the external volume of the globe will be almost the same.†

The correction now under consideration is thus the weight of 0.437 c.c. of air at the average temperature of the balance room. The density of this air may be estimated at 0.00122; so that the weight of 0.437 c.c. is 0.000533 gram. This is the quantity which must be added to the apparent weights of the gases. The former estimate was 0.00056 gram. The finally corrected weights are thus

$$H = 0.158531, \quad O = 2.51777;$$

and for the ratio of densities we have

$$15.882.$$

This corresponds to a mean atmospheric condition of pressure and temperature.

If we combine the above ratio of densities with Professor Morley's ratio of volumes, viz., 2.0002 : 1, we get, as the ratio of atomic weights, 15.880.

If we refer to the table, we see that the agreement of the first and

\* For greater security the tap was turned while the interior was under suction.

† For a spherical shell of glass of uniform thickness and with elastic constants following Poisson's law, the ratio of the difference of the internal and external expansion to either of them is  $4t/3a$ , where  $t$  is the thickness of the shell, and  $a$  the mean radius. In the present application the value of  $a/t$ , deduced from the measured circumference and from the weight of glass, is about 110.

[Perhaps an arrangement in which the *external* volume is directly measured would have been preferable. No allowance for expansion of water would then be needed.—Feb. 17.]

third series of hydrogen weighings is very good, but that the mean from the second series is decidedly lighter. This may have been in part fortuitous, but it is scarcely probable that it was so altogether. Under the circumstances we can hardly reckon the accuracy of the final results as closer than  $\frac{1}{30000}$ .

A word should perhaps be said upon a possible source of systematic error, viz., mercury vapour. There is no doubt that hydrogen passed over mercury takes up enough to cause a slow and superficial, but quite distinct, discoloration of sulphur over which it subsequently flows. In the experiments here recorded, the gas did not, indeed, flow over mercury in mass, but, inasmuch as mercury was used to secure the tightness of some of the joints, it is difficult to feel sure of its absence. Again, in evacuations conducted with a mercury pump can the vacuum be regarded as free from mercury vapour, which, it must be remembered, would not show itself upon the gauge of the Töppler? If both the hydrogen and the "vacuum" were saturated with mercury vapour, the result of the weighings would, according to Dalton's law, be free from its influence. The same may be said of any volatile impurity arising from the grease\* upon the stopcocks. As the matter stands, the results must, I think, be regarded as affected with a possible error amounting to a fraction of the weight of mercury vapour at the temperatures employed. But this is probably a very small quantity.

According to Hertz,† the vapour-pressure of mercury at 15° C. would be about 0.001 mm. If this be correct, the weight of mercury vapour in an atmosphere of hydrogen would be as a fraction of the latter

$$\frac{0.001}{760} \times 200 = \frac{1}{3800}.$$

It appears that in an investigation of hydrogen aiming at an accuracy of 1/10,000 the question of mercury vapour requires very careful consideration.

The accompanying table of results found by various experimenters may be useful for comparison:—

\* Composed of vaseline and beeswax.

† 'Wied. Ann.,' vol. 17, p. 199.

Name.	Date.	Atomic weights.	Densities.
Dumas .....	1842	15·96	—
Regnault .....	1845	—	15·96
Rayleigh .....	1888	—	15·884
Cooke and Richards .....	1888	15·869	—
Keiser .....	1888	15·949	—
Rayleigh .....	1889	15·89	—
Noyes .....	1890	15·896	—
Dittmar .....	1890	15·866	—
Morley .....	1891	15·879	—
Leduc .....	1891	—	15·905
Rayleigh .....	1892	—	15·882

In conclusion, I must express my obligations to Mr. Gordon, who has assisted me throughout. The work has been unusually tedious, partly from its inherent nature, requiring as it does a certainty of 0·1 milligram in the weighings, and still more from the constant liability to accidents, which may render nugatory a large amount of preparatory work.

*Presents, February 18, 1892.*

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FIG. 1.

