XLVI.—*On the Unit adopted for the Atomic Weights.*By **LOTHAR MEYER** and **KARL SEUBERT**.

THE dispute which arose immediately after Dalton first enunciated his atomic theory as to unit to which the atomic weights should be referred has for more than half a century divided the chemical world into two camps. Whilst Dalton, and more recently Leopold Gmelin, adopted the smallest atomic weight, that of hydrogen, as their unit, on theoretical and philosophical grounds, Wollaston and Berzelius preferred that of oxygen, partly because they laid less stress on theoretical considerations, but more especially from the purely practical point of view that most of the elements may be compared with oxygen directly, and with hydrogen only indirectly. After Dalton's unit—that of hydrogen—had universally gained the upper hand, for years the old dispute appeared to be settled, and it was to be hoped

that the more accurate investigation of the laws which govern the numerical coefficients of the atomic weights, begun in later times, might be carried out from one point of view. Unfortunately, however, it would appear that this reasonable hope is not to be fulfilled, for once more the old Wollaston-Berzelius theory has cropped up, although in an altered, but, as we consider, a more dangerous form.

As is well known, J. S. Stas,* from his own observations and from those of others, has deduced the highly probable conclusion that the atomic weight of oxygen is not quite 16 times as great as that of hydrogen, but rather about $\frac{1}{4.10}$ of its value less than 16 H. This follows from—

1st. The numerous gravimetric results obtained by gas analysis since Gay-Lussac and Von Humboldt's discovery, or, what amounts to the same thing, from Avogadro's law, and the experimental estimation of the vapour-densities of oxygen and hydrogen (see our calculation of atomic weights,† No. 1a, and Julius Thomsen's, *Ber.*, **3**, 927).

2nd. The synthesis of water by means of copper oxide (*loc. cit.*, No. 1c, d).

3rd. The relation of ammonium chloride to silver nitrate, and of both to silver (*loc. cit.*, Nos. 47 and 83), where the atomic weight of nitrogen (N = 0.87791. O) used in the calculation can be confirmed by the relation of both the chlorine and the metal to the nitrate (Nos. 131, 132, 133, 135).

Further, if perhaps with less certainty, from—

4th. The relations of the crystallised and anhydrous strontium chlorides to one another and to silver (Nos. 65, c, and 140).

5th. The relations of anhydrous and crystallised strontium chlorides to one another and to the sulphate (No. 197).

6th. The corresponding numbers for crystallised and anhydrous barium chlorides and silver (Nos. 66e and 141).

7th. The relations of both forms of barium chloride to the sulphate (No. 188d).

8th. From the relation of metallic aluminium to hydrogen and to water (Nos. 8c, d, and 144).

Estimations made according to sections 1 and 2, and yielding results whose accuracy is unquestioned, give a mean which coincides with the proportion $H : O = 0.06265 : 1 = 1 : 15.96$. This Stas also considers to be the nearest to the truth, whilst the rational proportion required by Prout's law $H : O = 0.0650 : 1 = 1 : 16.00$, which has been confuted by numerous observations, is sometimes quite outside the

* *Nouvelles Recherches sur les lois des Proportions Chimiques*. Bruxelles, 1865, p. 24, and elsewhere.

† *Die Atomgewichte der Elemente aus den Originalzahlen neu berechnet*. Leipzig, 1883.

experimental determinations, sometimes close to the limit. To an unprejudiced mind, therefore, having no bias in favour of either hypothesis, there can be no ground for preferring this simple relation to the number deduced from the mean of the observations. Moreover, if the whole number be accepted, the results obtained under sections 3 to 8 in almost all cases give results far less concordant than if the mean be taken, and in the determinations under section 3, the difference between the theoretical and observed numbers is actually greater than the experimental error.

As, however, the relation of the atomic weight of hydrogen to oxygen had not been so accurately ascertained as that of several other elements to one another, Stas, in order to show that Prout's hypothesis was quite untenable, reckoned out all his atomic weights according to *what he considered to be the incorrect supposition*, that the atomic weight of oxygen is precisely 16 times that of hydrogen. He pointed out that even on this supposition, beyond all measure favourable to Prout's hypothesis, it did not hold good for the other atomic weights. The adoption of Prout's figures by Stas in this case, which was merely hypothetical and done in order to ascertain whether conditions so favourable to Prout's view would confirm them or not, seems now often to be misunderstood, as indicating that the values $O = 16.00$ or $O = 15.96$ might be employed indifferently, which is not the case. Rather it is in the highest degree probable, if not certain, that whilst there is an error of from 0.03 to 0.05 in the coefficient $O = 16.00$, with the mean 15.96 the error is 0.01, or at most only 0.02.

As up to this time chemists had been accustomed to consider $O = 16.00$, and as Stas naturally only discussed the atomic weights recently determined by him, a choice had to be made between the laborious recalculation of all the atomic weights on the basis of the new values for O, Ag, Cl, &c., or to use the old numbers provisionally and to insert Stas' corrected atomic weights in the somewhat incongruous system. The latter easy but incorrect way was adopted by many chemists. This took place the more readily as most of the atomic weights used were rightly regarded as being more or less uncertain, so that a difference of $\frac{1}{410}$ of the weight of oxygen seemed of very little practical importance.

The reasonable hope that the recalculation of all the atomic weights would at least put an end to the old contention as to the most advisable unit weight to be adopted, has unfortunately not been fulfilled. Although it has been universally agreed to abandon the unit $O = 1 = 10$ or $= 100$ as used by Thomson, Wollaston, and Berzelius, and to adopt hydrogen as the unit, there is much difference of opinion as to how this is to be done. As with some few excep-

tions (*e.g.*, B, Al, No. 8c, *d*) the relation of the atomic weights to that of hydrogen can only be determined indirectly through oxygen; the accuracy of all the atomic weights must depend on that of oxygen. Acting on this consideration, we have in our recalculation of the atomic weights, referred to above, retained the unit $O = 1.00$ employed by Wollaston and Berzelius, along with the customary $H = 1.00$. So that in case of a new authentic estimation of the relation $H : O$, the numbers referred to hydrogen as unity can easily be corrected. Some little time ago G. F. Becker* calculated out all the atomic weights, on the supposition that $O = 16.00$, whilst F. W. Clarke†, has, as is the case in our calculations, considered hydrogen equal to unity; but, from a prejudice in favour of Prout's theory, he has constructed a table in which $O = 16$, whilst $H = 1.0023$. T. Sebelien‡ adopts the units employed by us ($H = 1$ and $O = 100$), although he also occasionally inserts numbers reckoned on the supposition that $O = 16$. W. Ostwald§ does not recognise the conclusion arrived at by Stas, that the coefficient $O = 16$ is too high, but makes use of the last five observations of Erdmann and Marchand,|| and rejects the three first, from which it follows that if $H = 1$ then $O = 16$ exactly, whilst the sum of all the researches of the authors named gives $O = 15.96$. J. D. van der Plaats¶ also is inclined to consider that $O = 16$, although he leaves the question open. W. Dittmar** has recalculated the atomic weights published by us (in which $H = 1$) on the supposition that $O = 16$ and $H = 1.0024$.

As a consequence of these different views, all the other atomic weights will differ by 0.25 per cent. of their value, amounting to as much as half a unit with the highest. Everyone will agree that this is undesirable, and also that the smallness of the difference increases the liability to mistakes and confusion, especially when authors give no indication as to what unit they adopt. It is more difficult to say how this inconvenience is to be avoided. In the first place, it must be allowed that both the proposed values of oxygen lie within the limits of experimental error; moreover, if some constant source of error should tend to lower the results, it would be permissible to adopt the maximum value 16.03 instead of the mean value $O = 15.96$. It is more dubious, however, to take the round number, 16.00, for which

* "Atomic Weight Determinations: a Digest of the Investigations published since 1814." Washington Smithsonian Institution, 1880.

† "A Recalculation of the Atomic Weights." Washington Smithsonian Institution, 1882.

‡ *Beiträge zur Geschichte der Atomgewichte. Preisschrift*: Braunschweig, 1884.

§ *Lehrbuch der allgemeinen Chemie*, Leipzig, 1884.

|| Our calculation No. 1d; see also Clarke, *loc. cit.*, p. 5.

¶ *Compt. rend.*, Jan. 5, 1885, 100.

** Tables to facilitate chemical calculations. 2nd edition. Glasgow, 1885.

there is no evidence, except Prout's refuted hypothesis. The secret or avowed preference for this hypothesis seems to be the true motive for adopting this number. We, however, willingly allow that there may be some grain of truth hidden in Prout's theory, but this does not alter the fact that this hypothesis, as at present set forth, is quite untenable. Up to the present time wherever determinations have been made with sufficient accuracy, it has always turned out that the atomic weights are not exactly whole numbers, and this result does not depend on the relation of hydrogen to oxygen. Say what one will, irrational or fractional numbers have been found for the most accurately determined atomic weights. That which is most worthy of note in Prout's hypothesis is best considered, and, indeed, less disadvantageously, when that relation of O to H is adopted which is in accordance with the most authentic observations. Thus it is worthy of remark, that the atomic weights of nearly a quarter of the elements are almost exact

Multiples of Half the Atomic Weight of Oxygen (O=15.96, H₂O=7.98).

Factor.	Product.	Observed atomic weights.	Differences.
1	7.98	—	—
2	15.96	O = 15.96	—
3	23.94	Mg = 23.94	—
4	31.92	S = 31.98	+ 0.06
5	39.90	Ca = 39.91	+ 0.01
6	47.88	Ti = 48.01	+ 0.13
7	55.86	Fe = 55.88	+ 0.02
8	63.84	—	—
9	71.82	Eksilicon	—
10	79.80	Br = 79.76	- 0.04
11	87.78	—	—
12	95.76	Mo = 95.90	+ 0.14
13	103.74	Ru = 103.50	- 0.24
14	111.72	Cd = 111.70	0.00
15	119.70	Sb = 119.60	- 0.10
16	127.68	—	—
17	135.66	—	—
18	143.64	Di = ?	—
19	151.62	—	—
20	159.60	—	—
21	167.58	Eb = ?	—
22	175.56	—	—
23	183.54	W = 183.6	+ 0.06
24	191.52	Os = ?	—
25	199.50	Hg = 199.80	+ 0.30
26	207.48	Bi = 207.3	+ 0.18
27	215.46	—	—
28	223.44	—	—
29	231.42	Th = 231.96	+ 0.54
30	239.40	U = 239.80	+ 0.40

multiples of half the atomic weight of oxygen or the equivalent weight as determined by the above-mentioned relation.

Such coincidences are worthy of note, but to rectify other atomic weights by them is as unjustifiable as to make the atomic weights round numbers.

For any one, however, who neither supports Prout's hypothesis nor holds the opinion that the observations coincide best with the relation $O : H = 16 : 1$, there seems to us to be not the smallest justification for preferring the value $O = 16$ to $O = 15.96$. For if 16 be taken as the atomic weight of oxygen rather than 1, or 10, or 100, it can merely be for the reason that it seems to be more convenient to take hydrogen as the unit. This in fact seems generally to be intended, but as it is thought that this relation to oxygen is not certain by some thousandths, it is considered better to use the round number 16 provisionally in place of that experimentally determined, viz., 15.96, although it then becomes necessary to make $H = 1.0025$, that is to take $\frac{3.2}{4.00}$ of the atomic weight of hydrogen as the unit. Such an irregular unit can only be allowable in the secret hope in the future fulfilment of Prout's law. No one would surely permanently burden science with such an anomaly.

Further it must be allowed that the atomic weights of all the other elements will vary in the fourth and following figures with that of oxygen, whilst their relative value in many cases has been definitely fixed to the fourth, and even in some cases the fifth place. No hypothetical considerations can alter this fact. Even if to-morrow the relation $O : H$ should be determined with certainty to within one or two thousandths of its value, and be found to differ from the number now accepted, all the other atomic weights would have to be recalculated.

We cannot see what advantage could be derived from provisionally calculating on the hypothesis that $H = 1.0025$ and $O = 16$. That the coefficients of oxygen, carbon, and a few others have been shortened to two figures can hardly be of such advantage as to justify the use of a unit which is not far from being absurd.

It has been asserted, however, that the errors introduced into calculations by considering $H = 1$ are less than the unavoidable experimental errors themselves, but even when this is the case it may well be asked why should even a small error be introduced when it can be avoided? Even without this are not our determinations already sufficiently burdened with sources of error of all kinds? It is, however, not universally the case that a disregard of these small fractional parts in the decimal place, which are ordinarily not taken into account in analyses, have no influence. Even when it causes no difference in most inorganic analyses, it is quite otherwise in the analysis of

organic bodies. No one, of course, would desire to make the calculation using $H = 1.0025$; but considering $H = 1$, and using either

$$\begin{aligned} O &= 15.96 \text{ and } C = 11.97 \\ \text{or } O &= 16.00 \text{ and } C = 12.00 \end{aligned}$$

differences are obtained in the calculation which under certain circumstances are actually greater than the differences in the composition of closely allied organic compounds. The following table gives the percentage of hydrogen and carbon for the paraffins containing 30 and 31 carbon atoms, and also of the alcohols and the acids derived from them (myricyl alcohol and melissic acid), and also the corresponding amounts of water and carbonic anhydride are given in percentages on the weights of the compounds analysed. The results in the columns headed *a* are reckoned for $O = 15.96$ and $C = 11.97$; those under *b*, $O = 16.00$ and $C = 12.00$.

	H ₂ O.		H.		CO ₂ .		C.	
	<i>a.</i>	<i>b.</i>	<i>a.</i>	<i>b.</i>	<i>a.</i>	<i>b.</i>	<i>a.</i>	<i>b.</i>
C ₃₀ H ₆₂	132.22	132.23	14.723	14.692	312.68	312.80	85.277	85.308
C ₃₁ H ₆₄	132.10	132.11	14.710	14.679	312.73	312.84	85.290	85.321
C ₃₀ H ₆₂ O	127.39	127.40	14.186	14.155	301.26	301.37	82.163	82.192
C ₃₁ H ₆₄ O	127.42	127.43	14.190	14.159	301.66	301.77	82.272	82.301
C ₃₀ H ₆₀ O ₂	119.46	119.47	13.303	13.274	291.94	292.04	79.620	79.646
C ₃₁ H ₆₂ O ₂	119.74	119.74	13.334	13.305	292.61	292.70	79.802	79.828

As is seen, the amount of water according to either calculation is almost identical, as the errors compensate one another; the hydrogen, however, varies by some hundredths, as does also the carbon, whilst the difference in the carbonic anhydride falls in the first place of decimals, and in the case of the hydrocarbons is actually greater than the difference between the hydrocarbons, differing by CH₂. This becomes even more noticeable if the percentages of carbon and carbonic anhydride calculated in both ways in a series of hydrocarbons are compared, as in the accompanying table.

	C ₂₄ H ₅₀ .	C ₂₅ H ₅₂ .	C ₂₆ H ₅₄ .	C ₂₇ H ₅₆ .	C ₂₈ H ₅₈ .	C ₂₉ H ₆₀ .	C ₃₀ H ₆₂ .
C { <i>a</i>	85.176	85.196	85.214	85.232	85.248	85.263	85.277
<i>b</i>	85.207	85.227	85.246	85.263	85.279	85.294	85.308
CO ₂ { <i>a</i>	312.310	312.384	312.452	312.516	312.575	312.630	312.681
<i>b</i>	312.426	312.505	312.588	312.632	312.690	312.745	312.796

It will be seen that calculations made under *a* or under *b* would lead to quite different interpretations of the analysis. If, for example, it be found by combustion that a hydrocarbon gave 312.5 mgrms. of CO₂ for every 100 mgrms. of substance, the advocate of Prout's law would consider that the results of the analysis would best be expressed by the formula C₂₅H₅₃, whilst according to Stas and his followers the analysis agrees with the formula C₂₇H₅₆. Now no one would of course think of determining the formula of such a body by the analysis alone, but in the choice of the formula it is customary to attach weight to the mean obtained from a series of concordant analyses, and this would lead to error if a mistake of a few thousandths in the atomic weight of hydrogen is considered as of no consequence.

Therefore, whoever agrees with us in considering that the proportion H : O = 15.96 : 1 = 1 : 0.06265, as being the result of the most accurate experimental determinations hitherto made, is more probably correct than O : H = 16.00 : 1 = 0.06250 as required by Prout's law, is guilty of gross inconsistency if he uses the atomic weights O = 16.00, C = 12.00, Cl = 35.46 or 35.5, &c. Of course these figures may be used in the laboratory for approximate calculations, or in preparation work, but they should be altogether discountenanced in calculations of the results of accurate analyses. We would ask the advocates of Prout's hypothesis to lay to heart the question as to whether the general acceptance of a universal basis for all the atomic weight determinations is not of more value than suppositions which in some few cases may possibly not be without foundation.

Every one allows that the relation advocated in this paper (and also all the other atomic weights referred to H = 1) is not yet established to within some few thousandths of its value. Let us then adopt without any reservation the mean value obtained by the concordant results of investigations which have been made in entirely different ways, and await in the future the further examination and establishment of these results by experimental methods. When this has been done we shall be ready amongst the first to make the necessary changes in the calculated values of the atomic weights.