III. *Researches on the Chemical Equivalents of Certain Bodies. By* Richard Phillips, *F.R.S., &c.*

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THE late Dr. Turner, in an elaborate memoir on atomic weights, contained in the Philosophical Transactions for 1833, observes, that "Dr. Prout's hypothesis as advocated by Dr. Thomson, that all atomic weights are simple multiples of that of hydrogen, can no longer be maintained," and he further asserts that hypothesis "to be at variance with the most exact analytic researches which have been conducted."

Although the experiments of Dr. Turner, and the inferences which he has drawn from them, agree very nearly with those of Berzelius, it still appeared desirable further to investigate this subject, and it occurred to me that the inquiry might be conducted in a mode not liable to some of the objections which may be urged against the processses usually adopted.

For the purposes of this investigation, I deem it peculiarly fortunate that Dr. Turner has adopted a whole number as the equivalent of silver, and on this account, as well as for other obvious reasons, I selected it as the basis for an inquiry respecting the equivalents of chlorine and some other elementary gases.

From Dr. Turner's experiments (Philosophical Transactions, 1829), it appears that 108 parts, or one equivalent of silver, yield 143·424 parts of fused chloride, which result coincides very nearly with the determination of Berzelius. Dr. Prout, however, has objected to the fusing of the chloride of silver, that during the operation, it yields hydrochloric acid, which is admitted by Dr. Turner to be the case, although he could not discover that chloride of silver, that had been dried at 300°, lost so much as a thousandth of its weight by subsequent fusion.

It seemed to me that the chance of error arising from the fusing of the chloride of silver might be entirely removed, and other advantages gained, by making an experiment with silver on a large scale, with such proportions of the substances employed as were deemed to be equivalents; and instead of calculating from the whole product of the fused chloride, to do it merely from the weight of such small portion only as might arise from the difference between theoretical views and experimental results.

With this purpose I purified some silver by dissolving it in nitric acid, precipitating by a chloride, dissolving the precipitate in ammonia, again throwing down the chloride and reducing it to the metallic state.

I could not discover any impurity in the silver thus obtained: I therefore dissolved 216 grains (2 equivalents) in nitric acid, and decomposed the nitrate formed, by

adding 108 grains of pure hydrochlorate of ammonia dissolved in water. I need hardly state, that the weight of the hydrochlorate was taken on the assumption, that this salt contains one equivalent of chlorine 36, one of azote 14, and four equivalents of hydrogen 4, equal 54. The chloride of silver precipitated was collected and washed on a filter, but instead of drying and fusing it, it was neglected, for a reason already assigned. Having ascertained that the solution from which this chloride was precipitated contained excess of hydrochlorate of ammonia, I added nitrate of silver to it and to the washings; the chloride of silver thus obtained was collected on a double filter of Chinese paper and washed and dried; it weighed 2·58 grains, a quantity too small to admit of any appreciable error from deficient drying in not subjecting it to fusion. Assuming that 144 of chloride of silver indicate 36 of chlorine, 2·58 grains will give 0·645 grain as the weight of the excess of chlorine in the two presumed equivalents of hydrochlorate of ammonia, and one half of this, or 0·322 grain, subtracted from 36, will reduce the equivalent of chlorine from that number to 35·678. On repeating this experiment I obtained 2·56 grains of chloride of silver, which brings the equivalent of chlorine to 35·680.

In order to bring under discussion the equivalents of other elementary bodies, I prepared some nitrate of silver from the pure metal; it was twice crystallized, and a portion of it, fused in a glass capsule, weighed 271·57 grains; adopting the equivalent weights above stated, and 8 for oxygen, 54 of hydrochlorate of ammonia should decompose 170 of nitrate of silver, and 86·263 of the hydrochlorate would therefore be required for the decomposition of the fused nitrate.

The solutions of these quantities of the salts were accordingly mixed, the precipitate was, as before, separated and washed, and on adding nitrate of silver to the filtered solution and washings, 1·74 grain of chloride of silver was obtained, indicating an excess of 0·435 grain of chlorine; now according to the assumed equivalents, 54 of hydrochlorate of ammonia contains 36 of chlorine, 86·263, the quantity employed in the experiment, therefore contained 57·508, from which, if we subtract 0·435, the excess, there will remain 57·073; if then 86·263 give 57·073, 54, the equivalent of hydrochlorate of ammonia, will contain 35·727 of chlorine instead of 36. This experiment was repeated with 357·34 grains of fused nitrate of silver, and 113·508 grains of hydrochlorate of ammonia; the excess of chlorine was 0·7 grain, which calculating as before, makes the equivalent of chlorine 35·667; and taking the mean results of the four experiments, viz. 35·678, 35·680, 35·727, and 35·667, we have 35·688 as the equivalent of chlorine.

Although Dr. Prout's hypothesis requires that the error, or the difference between 35·688 and 36 = 0·312, should not be divided among the various substances employed in the experiment, it may, nevertheless, be worth while to observe to what the error amounts when the numbers and quantities of the elements included in the operation are summed up: they are

1 equiv. silver . . .	108	
1 equiv. chlorine . .	36,	in the hydrochlorate of ammonia.
4 equivs. hydrogen. .	4,	one in the acid, three in the alkali.
6 equivs. oxygen . .	48,	one with the silver, five in the acid.
2 equivs. azote . . .	28,	one in the acid, one in the alkali.
14 equivs. weighing . .	224	

We have thus 14 equivalents of various elements, the sum of whose weights is 224, yet the mean error, or 0·312, without allowing for circumstances which I shall presently notice, is only about 1–717th part of the whole weight. It may also be remarked, that omitting the silver, and considering the other elements in their gaseous state, the error in volume will be comparatively less than that in weight; though it must at the same time be admitted that this difference is derived from the greater density of chlorine than of the other gases.

1 equiv. chlorine	36 grains	=	46 cubic inches, nearly.
4 equivs. hydrogen . . .	4 grains	=	186 cubic inches.
6 equivs. oxygen	48 grains	=	139 cubic inches.
2 equivs. azote	28 grains	=	93 cubic inches.
Total			464 cubic inches.

The weight of chlorine in error being, as already mentioned, 0·312 grain, or about 0·4 cubic inch, is only 1–1160th of the whole volume of the gases.

I have every reason to believe that all the substances which I used in the experiments above detailed, were of the greatest degree of purity; but I may observe that the admixtures most likely to occur in any of them would increase the quantity of the chlorine, or diminish that of the silver; and any substance producing either of these effects would erroneously diminish the equivalent of chlorine by increasing the weight of the precipitated chloride of silver, assumed to be derived from the error of the theory; thus hydrochlorate of ammonia always contains sufficient excess of acid to redden litmus paper, and any moisture or foreign metal which the nitrate of silver might contain would produce corresponding results.

From these experiments and considerations I am of opinion, that no material, and scarcely even any appreciable error can arise from considering the equivalents of hydrogen, oxygen, azote, and chlorine, as 1, 8, 14, and 36 respectively.

The specific gravity of oxygen and azote may be obtained by comparing their equivalent weights with the composition and density of atmospheric air. The mean of various experimental results of the weight of 100 cubic inches of air is about 31 grains, and this agrees very nearly with the determination of Dr. Prout. Now if pure air consist of 20 cubic inches of oxygen and 80 of azote, or of one equivalent of oxygen and 2 equivalents of azote, the weights of which are respectively 8 and 14, the 20 cubic inches of oxygen will weigh 6·88 grains, and the 80 of azote 24·08 grains,

giving 30·96 grains as the weight of 100 cubic inches of air; if, as more commonly admitted, air consists of 21 volumes of oxygen and 79 of azote, we shall have 7·224 grains as the weight of the oxygen, and 23·779 as that of the azote = 31·003 grains as the weight of 100 cubic inches of air; either of these determinations is sufficiently near to show, that we cannot be far wrong in estimating the weight of 100 cubic inches of oxygen at 34·4 grains, and the same volume of azote at 30·1 grains; and the weight of the equivalent of hydrogen being $\frac{1}{8}$ that of oxygen, and its volume twice as great, and the equivalent of chlorine being to that of oxygen as 36 to 8, while their volumes are equal, it follows that 100 cubic inches of hydrogen and chlorine will weigh respectively 2·15 and 77·4 grains, and the density of the four elementary gases in question, compared with air = 1, will be

Hydrogen	0·06935
Azote	0·97097
Oxygen	1·10968
Chlorine	2·49678

On comparing these densities with those stated by Professors Thomson, Turner, and Graham, it will be observed that they are less than those given by Dr. Thomson, which is accounted for by his having assumed that 100 cubic inches of air weigh 31·1446 grains, while they vary, but not very materially, from the weights assumed by Professors Turner and Graham, in being in some cases rather lighter and in others somewhat heavier.

	Thomson.	Turner.	Graham.
Hydrogen	0·0694	0·0690	0·069
Azote	0·9722	0·9727	0·976
Oxygen	1·1111	1·1025	1·1026
Chlorine	2·5000	2·4700	2·470