# XXI. *Experimental Researches on Atomic Weights.* *By* Edward Turner, *M.D. F.R.S. Lond. & Ed., Sec. G.S., Professor of Chemistry in the University of London.*

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THE present communication may be viewed as the continuation of an Essay on the Composition of the Chloride of Barium, which was honoured with a place in the Philosophical Transactions for the year 1829. In resuming the subject after such a long interval, I feel it right to apologize to the Society for the unfinished state in which that Essay has hitherto been left,—an omission far from voluntary, and entirely due to circumstances not subject to my own controul. In one point of view, however, the delay has been advantageous: it has afforded an opportunity to chemists to verify or correct the results contained in my first Essay, and has enabled me to repeat and extend my researches.

The object which I proposed to myself in commencing the present inquiry, was to re-examine some of those estimates which chemists have occasion to use continually as elements in their calculations, and to confide in as the foundation of their doctrines. With this view I undertook to determine the relative accuracy of the atomic weights which the British and Continental chemists respectively employ; and several circumstances induced me to begin by analysing the chloride of barium. Dr. Thomson, on whose experiments the British chemists relied, had obtained so many of his results by means of the chloride of barium, that any material error in the constitution of that compound would necessarily vitiate a large part of his table of equivalents; and if, on the other hand, the estimate of Dr. Thomson proved to be correct, an important error would be chargeable against Berzelius, whose numbers are very generally adopted on the Continent. The result of the inquiry is now well known: the source of fallacy, pointed out in my first communication, has been admitted by Dr. Thomson in the new edition of his System of Chemistry*, and he has accordingly changed the equivalent of barium from 70 to 68.

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* Seventh Edition, vol. i. p. 427.

The inevitable consequence of this change must be apparent to every one who is acquainted with the method of analysis so frequently resorted to by Dr. THOMSON. Many of the experiments described in his First Principles of Chemistry are now at irreconcilable variance with each other, and, if relied upon at all, subvert the conclusions which they once appeared to establish. Nor can those parts of his work which are not subject to this criticism be safely applied to the purposes of science. His view, for instance, of the composition of the compounds of oxygen with phosphorus, arsenic, and antimony, has been lately abandoned by himself*; and in the course of the present Essay I shall have occasion to prove, that the atomic weights which he has employed for silver and chlorine are likewise inadmissible. His analysis of sulphate of zinc, which was made, to use Dr. THOMSON'S own words, "the foundation on which he endeavoured to rear the whole subsequent doctrine of the atomic weight of bodies†," is peculiarly objectionable. Besides being vitiated by his error in the equivalent of barium, the oxide of zinc was determined by a method which involved an error in principle, and was in practice so complex as to be unfit for the extremely important object which it was intended to serve.

Having shown that the atomic weights current among British chemists, though in some instances correct or sufficiently approximative, have, as a whole, been adopted on insufficient and fallacious evidence, I shall now lay before the Society an account of experiments made for ascertaining the equivalents of lead, chlorine, silver, barium, and nitrogen.

### *Equivalent of Lead.*

BERZELIUS has made repeated and elaborate researches on the atomic weight of lead, and on the composition of its protoxide. His direct analysis of the oxide by reduction with hydrogen gas, simple as it appears, is liable to practical difficulties, the effect of which may be distinctly traced in the varying results of his experiments. Calculating from the two most discordant of the six analyses which BERZELIUS has published in his last Essay on this subject‡, the equivalent of lead, compared to oxygen as 8, will be 103·42 in one case, and 103·64 in the other. This difference, considering the simplicity of the method,

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* System of Chemistry, Seventh Edition.

† Annals of Philosophy, vol. xxvi. p. 363.

‡ POGGENDORFF'S Annalen, vol. xix. p. 314.

and the large quantities of oxide subjected to analysis, is very far greater than could arise in the hands of Berzelius from the mere accidents of manipulation. One source of error, which however he appears wholly or in great measure to have avoided, is the tendency of the oxide of lead to unite with the siliceous matter of the tube, and thus to escape reduction. Another, not improbable, cause of slight error is referrible to the facility with which spurious distillation ensues when gaseous matter passes over the surface of a hot liquid: by this means small quantities of lead may have been carried away by the hydrogen, and the loss in oxygen thereby rendered too large. Hence the probability is, that the real equivalent of lead is nearer to 103·64 than to 103·42.

Seeing no chance of procuring by means of hydrogen more uniform results than Berzelius obtained, I selected an entirely different method, dependent on the quantity of sulphate of lead which given weights of metallic lead and protoxide of lead respectively produce. The method consists of a few simple operations, which, with the requisite precautions, may be conducted with ease and accuracy. A solution of the best commercial acetate of lead was precipitated by carbonate of ammonia in excess, and the carbonate of lead, after being well washed with distilled water, was dissolved in nitric acid. From the nitrate, purified by repeated crystallization, the lead was again thrown down by carbonate of ammonia, and the carbonate reduced by black flux. The metal was washed, fused in a clean crucible, and poured on a clean stone: before being used, the superficial film of oxide was scraped off with a penknife. In the lead thus prepared I could detect no silver, copper, or other impurity: 100 grains of the metal, oxidized, converted into sulphate, and ignited, yielded to hot water a mere trace of sulphate of potash corresponding to what was introduced by the water and acids which were employed.

*Conversion of metallic Lead into Sulphate.*—The mode which I found most convenient for converting the metal into sulphate, was to introduce it into the requisite quantity of mixed nitric and sulphuric acid, diluted with an equal volume of water. The vessel employed for the purpose was a small bell jar, such as is used for collecting gases over mercury: when placed in an inclined position on the sand-bath, there was no danger of loss by spirting, the materials could be freely stirred, and the sulphate readily removed by help of a clean feather at the close of the process. The excess of the acids was next decanted into a platinum capsule two inches and a half in diameter, and expelled by evaporation. The sulphate of lead was then transferred to the same capsule, and gently evaporated to dryness, care being taken that some free sulphuric acid should be present. The capsule was then ignited by the flame of a spirit-lamp with a double wick, and its weight carefully taken before and after its contents were removed. The sulphate of lead should not be evaporated in a crucible, since otherwise the annoyance which Berzelius justly complained of, namely, loss by spirting, will be felt severely: by means of a capsule this inconvenience is entirely avoided. When the quantity of sulphate is abundant, it will be found convenient to transfer most of the salt to a crucible as soon as it is sufficiently dry to form a cake.

To prevent floating particles of dust from falling into the capsule during the evaporation, a disk of glass a foot in diameter was supported just above it, and the glass itself covered with a sheet of paper. Allowance was made for impurities contained in the water and acids. Each of these substances had been twice carefully distilled; but nevertheless, when evaporated, a trace of residue might be perceived: its quantity however was very minute. An ounce of nitric acid, four ounces of water, and 100 grains of sulphuric acid, (being twice as much of each as was employed in any single experiment,) were digested for a whole day on the sand-bath, and the residue was evaporated and ignited, every part of the operation being the same as in the conversion of lead into sulphate. The solid matter, consisting of the sulphates of lime and potash, amounted to 0·03 of a grain, half of which was therefore subtracted from the weight of ignited sulphate of lead in each experiment.

Another precaution, which ought not to be neglected in delicate atomic researches, was suggested to me by Dr. Clark of Glasgow. In the conversion of lead into a sulphate, the same substance is weighed in two different states, its density in one form being 11·358, and 6·298 in the other,—a circumstance productive of a small error, which is appreciable when the difference between the two densities is considerable. I have always avoided this error, when it was of sufficient amount to affect the second place of decimals, by using absolute instead of apparent weights, that is, adding to the weight of each substance in air, the weight of the air which they respectively displace.

The quantity of sulphate of lead yielded by a given weight of metallic lead is shown by the three following experiments, all corrections being allowed for. They were made after determining on the exact mode of manipulating by several previous trials:—

| | Lead. | | Sulphate. | | Lead. | | Sulphate. |
|---|---|---|---|---|---|---|---|
| Exp. 1.— | 79·968 | grains of metallic lead yielded | 117·097, | being the ratio of | 100 | to | 146·43 |
| Exp. 2.— | 63·257 | ——— | 92·607 | ——— | | | 146·398 |
| Exp. 3.— | 92·92 | ——— | 136·011 | ——— | | | 146·375 |
| The mean of the three experiments gave | | | | . . . . . . . . . . . . . . . . . . . . . . | 100 | to | 146·401 |

Four experiments of the same kind, published by **Berzelius**, gave the following numbers*:—

| | 1. | 2. | 3. | 4. | Mean. |
|---|---|---|---|---|---|
| Lead . . . | 100 . . . | 100 . . . | 100 . . . | 100 . . . | 100 |
| Sulphate . . . | 146·38 . . . | 146·4 . . . | 146·44 . . . | 146·458 . . . | 146·419 |

I adopt the ratio of 100 to 146·41 as being the mean of the whole.

*Conversion of Oxide of Lead into Sulphate.*—**Berzelius** has correctly shown that pure protoxide of lead cannot be prepared by decomposing the neutral nitrate by heat in a platinum crucible, since the crucible itself is always attacked, and the resulting oxide of lead intermixed with fine particles of platinum. To avoid this impurity, the oxide was prepared, as **Berzelius** recommends, from the subnitrate. To a cold solution of the neutral nitrate, pure ammonia was added in slight excess, and the white subnitrate collected on a filter, and dried. It was then introduced into a covered platinum crucible, and was heated for a full hour by a charcoal fire in an open grate, taking care to maintain it at a distinct red heat, but insufficient for fusion. The oxide was thus obtained in a pulverulent state, quite free from platinum, and of a pretty lemon-yellow colour. It ought to dissolve completely and easily in cold dilute acetic acid, yielding a colourless solution, which, on standing, does not deposite any brown particles of peroxide.

I may here mention the mode I adopt for weighing pulverulent or porous substances, so as to avoid the possibility of error from the condensation of air or moisture. The substance is well dried at the requisite temperature, and while hot is introduced into a small flask, capable of holding about an ounce of water, and of bearing a considerable temperature without breaking. The flask

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* Annals of Philosophy, vol. xv. p. 96.

and its contents are placed in the sand-bath, and while yet hot a tight cork is inserted: the whole, when cold, is weighed, the required quantity for experiment gently poured out, and the flask again restored to the balance. By this means the weight even of a deliquescent substance may be exactly determined. It is necessary before the first weighing to restore the equilibrium of the air within the flask by a momentary removal of the cork.

A given weight of carefully prepared protoxide of lead was dissolved in hot dilute nitric acid, yielding a perfectly clear colourless solution, and the lead was thrown down by an excess of sulphuric acid. After evaporating the clear liquid, and expelling the nitric acid, the precipitate was transferred into the platinum capsule, and the quantity of sulphate determined in the manner already described. I subjoin several of my results, calculated to 100 parts, with all corrections made: the actual quantity of oxide employed in almost every case exceeded 100 grains. The numerals indicate the order of time in which the experiments were made:—

| | 1. | 2. | 3. | 4. | 5. | 6. |
|---|---|---|---|---|---|---|
| Oxide | . . . 100 | . . . 100 | . . . 100 | . . . 100 | . . . 100 | . . . 100 |
| Sulphate | . . . 135·84 | . . . 135·71 | . . . 135·84 | . . . 135·75 | . . . 135·79 | . . . 135·78 |

On comparing the second with the first and third experiments, it was manifest that there was some source of fallacy, since the difference was fully twice as great as I expected to arise from mere error in manipulation. I speedily traced one error by finding, in the second experiment, that some nitrate had escaped decomposition, and by ignition had been left as oxide. This was indicated by a yellow stain, and was proved by digesting the ignited sulphate with dilute nitric acid, when lead was readily taken up. This inconvenience was effectually avoided in the later experiments, by carefully expelling the nitric acid before bringing the precipitate into the capsule, and moistening it with a distinct excess of free sulphuric acid during evaporation.

Another fallacy, which affects all the results above quoted, arose from traces of red lead remaining in the oxide and eluding detection by being decomposed in the hot, rather strong dilute nitric acid which was used as the solvent. I was led to suspect this error by the escape of globules of gas while the oxide was dissolving; and accordingly on taking up a portion in cold acetic acid, the peroxide was readily brought into view. It was this circumstance which induced me to express a belief, in a short report of these experiments to the British Association last June, that the equivalent of lead would be found rather higher than was then stated. Subsequent observation has justified that statement. Some pure protoxide of lead was prepared as before, and was then a second time kept at a red heat for a whole hour: it dissolved completely in cold dilute acetic acid; and 164·766 grains, treated as in the preceding experiments, yielded 223·943 of sulphate, being in the ratio of 100 to 135·92. Every part of this experiment was successfully performed, and I therefore confide in it as representing the true constitution of sulphate of lead. It is accordingly composed of

| | | | |
|---|---|---|---|
| Protoxide of lead | 164·766 grs. | 100 | 73·575 |
| Sulphuric acid | 59·177 grs. | 35·92 | 26·425 |
| | 223·943 | 135·92 | 100·000 |

Assuming, agreeably to the experiments already described (page 527), that 100 parts of metallic lead yield 146·41 of the sulphate, or that 100 of the sulphate contain 68·301 of metallic lead, it follows that the oxide consists of

| | | |
|---|---|---|
| Lead | 68·301 | 103·6 |
| Oxygen | 5·274 | 8 |
| | 73·575 | 111·6 |

The equivalent of lead, according to these results, may be safely estimated at 103·6. It cannot be so high as 104, as is supposed by some British chemists; for according to the numbers current in this country, 100 of metallic lead ought to yield 146·16 of sulphate, instead of 146·41 found experimentally; and agreeably to the same estimates, 100 of the protoxide of lead should yield 135·72, instead of 135·92, the experimental quantity.

### *Equivalent of Chlorine.*

The most conclusive experiments I have met with on this subject, are those of Berzelius. He obtained from 100 parts of chlorate of potash 39·15 of oxygen and 60·85 of chloride of potassium; and he also found that 100 of chloride of potassium correspond to 192·4 of chloride of silver. According to my own experiments, which coincide very closely with those of Berzelius, 100 parts of silver yield 132·8 of the chloride. From these data it follows that the equivalent of chlorine is 35·45.

*Chloride of Lead.*—To compare with this number the equivalent of chlorine deduced by a different process, some pure carbonate of lead was dissolved in muriatic acid diluted with boiling water, and the purity of the chloride ensured by repeated crystallization. The dry crystals were then fused in a tube filled with dry chlorine gas; and while the chloride was yet warm, the chlorine was displaced from the tube by dry carbonic acid gas. The resulting chloride of lead was colourless, and dissolved completely in hot water. The analysis was performed by decomposing the solution of chloride of lead by carbonate of soda, acidulating the clear solution with nitric acid, and precipitating with nitrate of silver. The carbonate of lead, after being washed, was dissolved in acetic acid, and tested for chlorine. The quantity of chlorine was inferred from the quantity of chloride of silver, and that of lead from the quantity of chlorine. After a few repetitions I obtained uniform results, and subjoin the proportions of the two most successful experiments:

| | 1. | | 2. | |
|---|---|---|---|---|
| Lead | 19·582 | 103·6 | 23·099 | 103·6 |
| Chlorine | 6·708 | 35·48 | 7·901 | 35·43 |

These results, then, give an equivalent for chlorine closely agreeing with that calculated from the analysis of chlorate of potash as above quoted from Berzelius. They are, at the same time, entirely inconsistent with the atomic weights current in this country. For, supposing 104, 36, and 110 to be the respective equivalents of lead, chlorine, and silver, it follows that 100 parts of the chloride of lead should yield 104·28 parts of chloride of silver, instead of 103·24 as given by experiment,—a difference very far beyond the reasonable limits of error.

*Oxide of Mercury.*—Wishing to obtain still further evidence respecting the ratio of the atoms of chlorine and oxygen, I determined on performing a careful comparative analysis of the binoxide and bichloride of mercury. I at first employed some red oxide prepared by myself from the nitrate; and though the analyses made with that substance are subject to a slight error, yet as the side on which the error lies is apparent, it will not be unprofitable to record them. A quantity of oxide of mercury was decomposed in a porcelain retort by a red heat, and the mercury was received in distilled water. It was well boiled successively with muriatic acid, potash, muriatic acid, and distilled water. The pure metal was oxidized by very pure nitric acid, and the nitrate decomposed by heat, the temperature at the last being urged so fully to a decomposing heat, that some metallic mercury sublimed. This was done to decompose every trace of nitric acid, and it succeeded to a very great extent; but when considerable quantities of the oxide, such as 150 grains, were decomposed by heat, the sublimed mercury exhibited a faint yellow ring, indicative of a small quantity of nitric acid. Even digestion with a solution of potash did not prevent this appearance.

The method of analysis was by the direct action of heat. A given weight of the red oxide, previously exposed to a heat of 600° to expel all trace of metallic mercury, was introduced into a tube of German glass, five eighths of an inch wide, and about ten inches in length; and the oxide was decomposed by the flame of a spirit-lamp, the remainder of the tube being kept cool by moistened paper. The gas as it escaped passed through a bent narrow tube, containing pieces of silver, and ultimately passed over a surface of gold-leaf: this tube was weighed at the beginning and close of each experiment, but in general the quantity of mercury conveyed into it was not appreciable. When the decomposition was complete, the tube was filled with dry carbonic acid gas, and the metal was again distilled. The subjoined numbers contain the results of two experiments performed after acquiring experience in the manual part of the method by several previous trials:

| | 1. | | 2. | |
|---|---|---|---|---|
| Mercury | 144·805 grs. | 200·768 | 125·98 grs. | 199·968 |
| Oxygen | 11·54 grs. | 16 | 10·08 grs. | 16 |

The figures at the left hand of each bracket indicate the quantities actually observed. The oxide employed in the two analyses was prepared at different times. Neither portion was wholly free from nitric acid; and hence it is apparent, as the loss was thereby rendered greater than it ought to be, that the real equivalent of mercury must exceed 200·768.

I next proceeded to analyse peroxide of mercury prepared by heat; and for that purpose a number of pure scales was selected from among a large sample of commercial oxide. On exposure to a temperature of 600°, a portion of metallic mercury was expelled, and the colour of the oxide brightened; indeed, every specimen of oxide which has fallen into my hands contained some free mercury, separable by heat, and due, I presume, to the deoxidizing agency of light. A similar remark was made some years ago by Professor Daniell. The sample analysed contained likewise 0·01 per cent. of fixed matter, which was silica or peroxide of tin coloured by iron, together with a little lime. Allowance was of course made for it. The following is the result of two careful analyses:

| | 1. | | 2. | |
|---|---|---|---|---|
| Mercury | 173·561 grs. | 200·94 | 114·294 grs. | 200·93 |
| Oxygen | 13·82 grs. | 16 | 9·101 grs. | 16 |

From this it would seem that the equivalent of mercury is not 200 as commonly believed by British chemists, but about 201. For the moment, I adopt this number, and will revert to the subject afterwards.

*Bichloride of Mercury.*—The corrosive sublimate of commerce was purified by repeated crystallization from distilled water, and was then well dried at its subliming temperature. It might in that state be sublimed without giving any trace of humidity. Of this chloride 137·595 grains were dissolved in warm water, and directly decomposed by nitrate of silver; and the chloride of silver was washed with water acidulated with nitric acid, and amounted in the fused state to 144·374 grains, equivalent to 35·659 of chlorine. The bichloride of mercury would hence seem to be composed of

| | | |
|---|---|---|
| Mercury | 101·936 | 201 |
| Chlorine | 35·659 | 70·31 |

giving 35·16 as the equivalent of chlorine. This result led me to suspect some imperfection in the method of analysis; and I accordingly found that some of the bichloride of mercury is apt to combine with the chloride of silver, and being expelled when the latter is fused, a loss of chlorine is occasioned. To avoid this error, the bichloride was decomposed by lime, which was prepared from Carrara marble, and was quite free from muriatic acid. The requisite quantity of lime, previously slaked, was mixed with a little warm water, and the solution of a known weight of corrosive sublimate gradually added, shaking the mixture after each addition. After a short digestion and filtration, the liquid was neutralized by nitric acid, and the chlorine determined by nitrate of silver in the usual manner. Every trace of muriatic acid may thus, without the necessity of boiling the materials together, be transferred to the lime and rendered soluble, while the oxide of mercury, of an orange colour, is left with the excess of lime. In this way I obtained the three following ratios:—

| | 1. | | 2. | | 3. | |
|---|---|---|---|---|---|---|
| Mercury | 113·441 | 201 | 113·149 | 201 | 112·535 | 201 |
| Chlorine | 39·748 | 70·428 | 39·723 | 70·565 | 39·433 | 70·43 |

According to these results we obtain 35·214, 35·28, 35·26 as the equivalent of chlorine.

*Calomel.*—The proto-chloride, though much more stable than the protoxide of mercury, is very subject to change. I believe it is impossible to sublime calomel without a portion being resolved into mercury and corrosive sublimate; and after washing calomel, so as to remove the adhering bichloride, the heat subsequently required for rendering it quite dry causes a fresh production of corrosive sublimate. I selected for analysis the pulverulent white calomel prepared by Mr. Howard, and dried it by exposure to a continued heat of 300° Fahr.; at which temperature it undergoes no appreciable decomposition, and contains only a trace of moisture. But that trace of humidity affects the ensuing results with a small error, the tendency of which is to make the equivalent of chlorine smaller than it is. The following are the ratios of three careful analyses, which were made by means of lime, as in the analysis of corrosive sublimate.

| | 1. | | 2. | | 3. | |
|---|---|---|---|---|---|---|
| Mercury | 100·048 | 201 | 95·154 | 201 | 76·565 | 201 |
| Chlorine | 17·602 | 35·361 | 16·721 | 35·32 | 13·473 | 35·37. |

It will now be convenient to compare together the numbers expressive of the equivalent of chlorine as determined from the four sources above enumerated: these are

| | From Chlorate of Potash, (Berzelius.) | Choride of Lead. | Bichloride of Mercury. | Protochloride of Mercury. |
|---|---|---|---|---|
| Equivalent of chlorine | 35·45 | 35·45 | 35·28 | 35·35. |

The equivalent of chlorine is thus limited by the numbers 35·28 and 35·45, and the mean is 35·33. Though this number has been obtained by four distinct methods, yet there is one element of the calculation common to all, namely, the composition of chloride of silver. Should any material error exist in this fundamental point, a doubt may still be raised respecting the equivalent of chlorine; but if we can rely on the constitution of the chloride of silver as here employed, then I should feel no hesitation in confining the equivalent of chlorine within the limits which have just been assigned. Now it happens that on this very question a doubt has been raised by my friend Dr. Prout, whose remarks are always pertinent, being founded on careful observation. Chloride of silver, as Dr. Prout informs me, invariably gives out muriatic acid at a certain stage of drying; and he suggests whether the loss may not be sufficient to influence the atomic weight of chlorine. Into this point I have carefully examined. Nitrate of silver was precipitated by muriatic acid in excess, was well washed with warm water, and set to drain in a dark closet. Exposed to light it acquired an acid reaction; and heated in contact with litmus-paper, the colour was reddened, even though not at the same time under the influence of light. A portion was introduced into a clean retort, and heat applied so as to dry it in that situation, day-light being excluded: the water which thus came over was quite neutral, and the chloride was at length left quite white and dry, without a trace of acid being lost. The same experiment was repeated with the same result. I hence consider it as certain that pure chloride of silver may be completely dried at 300° Fahr. without loss of any acid, if light and organic matter be excluded. On heating this dry and white chloride in a test-tube, a portion of acid sufficient to redden litmus was given out, just as the colour of the chloride darkened in the act of fusing. This phenomenon is constant. To try the amount of the loss, a quantity of pure chloride of silver was well dried at 300° Fahr.; and in one experiment forty-one grains, and in another ninety grains, were fused in a platinum crucible. In neither case did the loss amount to an appreciable quantity: I could not satisfy myself that it reached 0·01 of a grain. In these trials, however, the dry chloride was corked up in the weighing flask while still warm; for if allowed to cool in the open air, it absorbs a little air and moisture, and then on being fused a slight loss is perceptible. These experiments have been preferably made with chloride of silver thrown down from the nitrate by muriatic acid: the results are similar with any pure chloride; but when precipitated by sea-salt, it is apt, unless very carefully washed, to retain a little chloride of sodium, and then I believe the developement of acid is more easy than when the chloride of silver is quite pure.

The foregoing experiments have given me the most perfect conviction that my estimate of the constitution of hornsilver, deduced from the researches published in my last Essay, is in no wise vitiated by the fact noticed by Dr. Prout. But in order, on a point of so much practical and theoretical interest, not to omit any evidence which might elucidate the subject, I endeavoured to analyse corrosive sublimate by directly ascertaining the quantity of mercury which it contains. For this purpose a quantity of grain tin was oxidized by nitric acid, and the resulting oxide, after being washed and ignited, was reduced by charcoal. The pure tin, after being granulated and washed, was dissolved in strong muriatic acid. The solution was colourless and transparent, and an excess of acid was added to it. The reduction of the bichloride was thus effected. A given weight of the compound was dissolved in a small quantity of hot water acidulated with muriatic acid, and the protochloride of tin, likewise hot, was added in excess. A tube twelve inches long, surrounded by a moist cloth, was then attached to the flask containing the mixture, and ebullition was kept up for a few minutes, the extremity of the tube being closed by the finger. This precaution was taken in order to prevent, as far as possible, loss of mercury by the ebullition which is required for collecting together the finely divided metal. Most of the mercury was thus obtained in one bright globule: it was fully washed by tepid water acidulated with muriatic acid, and the decanted washings were set aside till the suspended particles had subsided. The mercury was ultimately collected on a double filter, which was dried under a bell-jar with a vessel of sulphuric acid, the air at the close being rarified. The two most successful experiments supply the following numbers:—

| | 1. | | 2. | |
|---|---|---|---|---|
| Mercury | 44·782 | 201 | 73·09 | 201 |
| Chlorine | 15·90 | 71·366 | 25·97 | 71·413. |

I should be unwilling to adduce these experiments as giving an exact view of the composition of corrosive sublimate, because the chlorine is inferred from the quantity of mercury collected, and the mercury is obtained by a method in which a small loss is, I believe, unavoidable. They answer the purpose, however, which they were intended to serve. For in giving 35·67 as the equivalent of chlorine, they show the highest practicable number; because, since the mercury obtained was pure and dry, its quantity could not represent less than was present in the compound subjected to analysis. It may have contained more, but not less mercury than was collected; and any quantity to be added to that above given would proportionally diminish the quantity of chlorine. Thus, if these analyses are at all trustworthy, they prove that the equivalent of chlorine may be less than 35·7, but that it cannot be greater.

There seems, therefore, to be no reason to call in question the methods which have been used to find the equivalent of chlorine. The real number, as above stated, is to be sought within a range extending from 35·28 to 35·45. This range may be much narrowed by facts supplied by other experiments. Were 35·35 assumed as the equivalent of chlorine, 107·78 would be the equivalent of silver, deducible from the composition of chloride of silver; but this number for silver is inconsistent with the analysis of nitrate of silver to be afterwards mentioned, and consequently the hypothesis which led to it is inadmissible. By a similar line of reasoning the equivalent of chlorine may be brought within the limits 35·4 and 35·45. I am disposed to select 35·42 as agreeing closely with my own results, coinciding with the number given in the most recent tables of BERZELIUS, and as giving a convenient number for silver.

### *Equivalent of Silver.*

It appears, at first sight, such a simple operation to prepare oxide of silver, and to reduce that oxide by heat, that my first attempts to ascertain the atomic weight of silver were made with that compound. It was soon apparent, however, by want of uniformity in my results, that some fallacy existed; and after numerous unsuccessful efforts to detect it, I abandoned the method altogether. The examination of sulphuret of silver was likewise begun, and subsequently abandoned for a similar reason. The analysis of the oxide was thought of as a means of comparing the equivalents of oxygen and chlorine through the medium of silver; but as this object has been attained by other means, it is easy to infer the equivalent of silver by the constitution of the chloride. In the belief that 100 parts of silver unite with 32·8 of chlorine, the atomic weight of silver will be 107·92, 108, or 108·08, according as we adopt 35·4, 35·42, or 35·45, as the equivalent of chlorine. As the whole number has as equal a chance of being correct as either of the others, it may be adopted with propriety, and is certainly a very close approximation.

### *Equivalent of Barium.*

The atomic weight of barium may be calculated from my analysis of the chloride of barium already published in the Philosophical Transactions. According to the proportions there stated, 100 parts of the chloride consist of 65·984 of barium and 34·016 of chlorine; the equivalent of barium is therefore 68·7, that of chlorine being 35·42. The analysis of Berzelius differs slightly from mine, giving 68·53 as the equivalent of barium. I adopt 68·7, as confiding in the indications of frequently repeated experiments; but at present I have no other proof that this number is more exact than that employed by Berzelius; it appears certain that 69 is too high, and that 68 is too low, being incompatible with our analyses.

### *Equivalent of Nitrogen.*

I have endeavoured to ascertain the equivalent of nitrogen by the analysis of the nitrates of silver, lead, and baryta.

*Nitrate of Silver.*—Pure silver was oxidized and dissolved in nitric acid, and the concentrated hot solution set aside. In cooling, it deposited numerous transparent thin tabular crystals, which were fused, redissolved in water, evaporated, and again kept for some time in a state of fusion. The fused nitrate was quite colourless, and dissolved in water without the least turbidity. It was analysed by solution in water and precipitation by muriatic acid; the whole was transferred to a porcelain capsule, evaporated on the sand-bath to perfect dryness, being protected at the same time from dust and light, and was then fused. The impurity introduced by the acid and water employed in each analysis amounted to 0·01 of a grain, which was subtracted from the whole weight obtained. The following is the result of two very successful analyses, made after several preliminary and less satisfactory experiments:—

| | 1. | | | 2. | | |
|---|---|---|---|---|---|---|
| Nitrate of silver | 124·892 grs. | 100 | 118·544 | 97·992 grs. | 100 | 118·5 |
| Fused chloride of silver | 105·355 grs. | 84·357 | 100 | 82·695 grs. | 84·389 | 100. |

It may therefore be inferred, as a mean of these closely corresponding ratios, that 100 parts of the fused chloride corresponds to 118·522 of the fused nitrate of silver. By the analysis of chloride of silver, 100 parts contain 75·3012 of metallic silver, corresponding to 80·87 of oxide, the equivalent of silver being 108.

Hence 118·522 parts of nitrate of silver contain 80·87 of oxide and 37·652 of nitric acid; and on subtracting from this quantity of acid five times the oxygen of the oxide of silver, viz. 27·844, there remain 9·808 of nitrogen. The equivalent of nitrogen, calculated from these numbers, is 14·09.

*Nitrate of Lead.*—Carefully prepared nitrate of lead was reduced to a very fine powder, and then dried at a temperature of 300°. It is not safe to expose this salt to a temperature much beyond 300° Fahr., as it is apt, when so heated, to suffer partial decomposition: perfect desiccation must be secured by fine levigation, and the continued action of a comparatively moderate heat. Known quantities of the salt were then dissolved in distilled water, and decomposed by an excess of sulphuric acid; and the resulting sulphate was collected in the same manner and with the same precautions as were described in a former part of this Essay, (page 526–528.). The following is the result of three successful experiments:—

| | 1. | | 2. | | 3. | |
|---|---|---|---|---|---|---|
| Nitrate of lead | 132 grs. | 109·312 | 99·888 grs. | 109·31 | 130·122 grs. | 109·3 |
| Sulphate of lead | 120·755 grs. | 100 | 91·38 grs. | 100 | 119·05 grs. | 100. |

As a mean of these analyses, it follows that 109·307 parts of nitrate yield 100 of sulphate of lead; and it has already been shown that the latter contain 73·575 parts of oxide, and 68·301 of metallic lead. From these data, and by the same mode of reasoning as was applied to nitrate of silver, it follows that 14·201 is the equivalent of nitrogen.

*Nitrate of Baryta.*—This salt was prepared from the native carbonate, and was purified by repeated crystallization; no impurity could be detected in it, and it was especially examined, by well known tests, for lead and strontia. It was converted into sulphate in the same manner and with the same precautions as were explained in the experiments with lead. It was dried by being reduced to a fine powder, and exposed to a temperature of 500°.

The following is the result of three satisfactorily conducted analyses, performed after several preparatory trials:—

| | 1. | | 2. | | 3. | |
|---|---|---|---|---|---|---|
| Nitrate of baryta | 92·83 grs. | 112·06 | 97·38 grs. | 111·99 | 121·391 grs. | 112·035 |
| Sulphate of baryta | 82·84 grs. | 100 | 86·955 grs. | 100 | 108·35 grs. | 100. |

As a mean of these analyses it appears that 112·028 parts of nitrate yield 100 of sulphate of baryta, which contain 65·669 of baryta and 58·8195 of barium. Hence, as in the former instances, it may be calculated that 14·17 is the atomic weight of nitrogen. It is assumed in this calculation that 68·7 is the equivalent of barium, and that 100 parts of chloride of barium contain 65·984 of barium, and correspond to 112·18 of sulphate of baryta.

The equivalent of nitrogen thus appears to be somewhere between the numbers 14·09 and 14·2, and the mean is 14·15, which corresponds closely with the number selected by Berzelius from his analysis of nitrate of lead. It must be admitted, however, that this mode of deducing the equivalent of nitrogen is not a desirable one, since the slightest error in the equivalents of silver, lead, and barium is multiplied five times in estimating the composition of nitric acid. The united testimony of three independent sets of experiments (or rather four, including the analysis of Berzelius,) serves to diminish the force of this objection; but still chemists must give a preference to the more direct method, founded on an exact determination of the densities of oxygen and nitrogen gases, such as we anticipate from the labours of Dr. Prout.

### *Equivalent of Sulphur.*

I have not yet entered upon a systematic investigation of the atomic weight of sulphur, but merely purpose, on the present occasion, to extract the information which flows incidentally out of the researches in which I have been occupied. It has been shown that 100 parts of sulphate of lead consist of 26·425 of sulphuric acid and 73·575 oxide of lead, which last contain 5·274 of oxygen. From these data, coupled with the known atomic constitution of sulphuric acid, it follows that this acid is composed of

| | | |
|---|---|---|
| Sulphur . . . . . . . | 10·603 . . . | 16·083 |
| Oxygen . . . . . . . | 15·822 . . . | 24 |
| | 26·425 | 40·083 |

Similarly, from the estimates above given, it follows that 100 parts of sulphate of baryta consist of 34·331 of sulphuric acid and 65·669 of baryta, which contain 6·8495 of oxygen. Hence it follows that sulphuric acid is composed of

| | | |
|---|---|---|
| Sulphur . . . . . . . | 13·7825 . . . | 16·097 |
| Oxygen . . . . . . . | 20·5485 . . . | 24 |
| | 34·3310 | 40·097. |

These estimates agree closely with that of **Berzelius**, deduced by a similar method. Though in some measure subject to the criticism already referred to in the foregoing observations on nitrogen, they leave no doubt on my mind of the equivalent of sulphur being rather more than exactly double the equivalent of oxygen. I hope, however, to examine this point more narrowly on a future occasion.

### *Equivalent of Mercury.*

The principal experiments which have been published on the equivalent of mercury are by **Sefström** and **Donovan**. According to three analyses of the red oxide of mercury by **Sefström**, the results of which are given in the Annals of Philosophy*, 16 parts of oxygen unite with 202·78, 202·54, 200·24 of mercury. **Donovan** found the peroxide to consist of 16 parts of oxygen and 204·6 of mercury, and the protoxide of 8 of oxygen and 194·2 of mercury. It is difficult from such very discordant results to strike any mean which should be moderately trustworthy. **Donovan's** analysis of the protoxide is of no use, as that compound is so very unstable as to be wholly unfit for atomic researches; and his analysis of the peroxide must certainly be erroneous, owing, perhaps, to his having overlooked the presence of metallic mercury in the peroxide which he examined. Even the analyses of **Sefström** indicate that the equivalent of mercury lies within the somewhat wide range extending from 200·24 to 202·78. The number may be brought within a narrower limit by the researches already described in this Essay. The equivalent deduced from the analyses of the red oxide is 200·94 and 200·93: the three analyses of calomel, taking the atomic weight of chlorine as 35·42, give 201·28, 201·3, and 201·57, of which the mean is 201·38, as the equivalent of mercury; and the numbers deducible from the three analyses of corrosive sublimate are 201·78, 202·16, and 202·18, of which 202·04 is the mean. Thus the equivalent is included within the numbers 200·93 and 202·18. Moreover, it will be remembered, that on calculating the equivalent of chlorine on the hypothesis of 201 being the real equivalent of mercury, an error was committed, which involved the alternative, either that 201 was too low, owing to a slight error in the analysis of the oxide of mercury, or that all the analyses of calomel and

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* iii. 355.

corrosive sublimate were inaccurate. The latter supposition is very much less probable than the former. With regard to the relative value of the experiments made with calomel and corrosive sublimate, I rely most on the analyses of the latter, since it is much more stable as regards the action of heat, and hence more certainly obtained in a pure state than calomel. I therefore infer that 202 may be considered as a close approximation to the real equivalent of mercury.

Before closing this communication, I will avail myself of the opportunity to make a few remarks on the employment of filters. In so far, indeed, as respects the experiments which have been described in the present and preceding Essay, the discussion is not very material, since most of the principal facts have been ascertained by processes independent of filtration; but in reference to analysis in general, the subject is very important. In my own researches I am in the habit of determining the weight of substances collected on a filter in one of three different ways. One of these, introduced by BERZELIUS, consists in burning the filter in a platinum crucible, and deducting the weight of its ashes. This method is peculiarly applicable to the analysis of minerals, where such substances as silica, alumina, and lime are frequent. Even some substances of easy reduction, such as peroxide of iron and sulphate of baryta, may be safely treated in the same way; but in these cases it is advisable not only, as usual, to separate the mass of the precipitate from the filter before setting it on fire, but to moisten both with a little nitric acid, and to ensure very free exposure to the air during the burning of the paper and the subsequent ignition. For such purposes I commonly use some excellent Swedish filtering paper, kindly procured for me by BERZELIUS.

Another method is that of the double filter, introduced by Dr. THOMSON, which I have used in all the experiments where filtration is spoken of in the present and former communication. Both BERZELIUS and Dr. THOMSON himself seem inclined to doubt the accuracy of this method; and it is certainly liable to objection, except with certain precautions and with very compact filtering paper. The paper which I use for the double filter is considerably thicker than the Swedish paper, and of such compact texture that recently precipitated oxalate of lime, or sulphate of baryta thrown down by GLAUBER's salt in a neutral solution of the chloride of barium, may be filtered by it. The precautions employed are these. The paper, folded into filters, is macerated in dilute nitric acid for two days, is then fully washed with warm distilled water, and dried at a temperature of about 212° FAHR. After acquiring its hygrometric moisture, two of the filters of nearly the same weight are poised against each other, and any small difference marked in pencil on the lighter one. Before being used, a pin-hole is made in the outer filter, in order that any accidental imperfection in the inner filter should be made apparent. After filtration both filters are dried at the same temperature, and are afterwards allowed to recover their hygrometric moisture completely before removal to the balance. In repeated trials I have found a pair of filters to recover, after use, their original relation in weight to within the 100dth part of a grain; nor have I ever noticed a greater deviation than may well be expected in every process where filtration is concerned. Additional testimony of the same kind will be found in my Essay printed in the Philosophical Transactions for 1819, where, in two sets of experiments, the same point is investigated by the use of double filters and by evaporating the precipitate to dryness without filtration. The series with silver, moreover, are interesting in reference to the remarks of Dr. PROUT above noticed (p. 534); for it is manifest from those results that chloride of silver may be collected on paper and dried, (in my experiments the filters were dried in a dark, warm air-closet,) without appreciable loss of acid.

A third method consists in employing a single filter, which is dried before and after filtration at some fixed temperature, as at 212° FAHR.; and when so dried is inclosed in a light silver vessel, the cover of which is tightly fitted by grinding. The filter may thus be deliberately weighed without absorbing moisture during the operation. In case of its being inconvenient to employ an uniform temperature, the filter may be dried at a variable heat, be allowed to absorb hygrometric moisture, and afterwards kept at about 60° FAHR. for two hours in a closed bottle, the bottom of which is covered with pulverized quicklime. In this method, while operating at least with paper of British manufacture, it is essential, more so than with the double filter, to have previously macerated the filter in dilute acid; for all such paper, which I have examined, contains lime.

I now, in conclusion, subjoin a list of the atomic weights ascertained by the researches described in the present communication, and add for the convenience of comparison the corresponding numbers of Berzelius from his latest table of equivalents*, as well as those published by Dr. Thomson in his First Principles of Chemistry.

| | Thomson. | Berzelius. | Turner. |
|---|---|---|---|
| Lead | 104 | 103·5598 | 103·6 |
| Silver | 110 | 108·1285 | 108 |
| Chlorine | 36 | 35·412 | 35·42 |
| Barium | 70 | 68·5504 | 68·7 |
| Mercury | 200 | 202·5315 (Sefström.) | 202 |
| Nitrogen | 14 | 14·1628 | 14·15 |
| Sulphur | 16 | 16·0932 | 16·09 |

The equivalents fixed on by Berzelius are in general substantially the same as mine. I have had continual opportunities of witnessing the extreme care which he employs in his experiments, as well as the fairness with which he reports them. His estimates, when directly drawn from his own experiments, are in general very close approximations. The chief difference between us is in the mode of representing equivalents: Berzelius strikes a mean of his results, and then calculates the atomic weight to a number of decimal places, which, in general, far exceed the degree of approximation justified by experiment; whereas I calculate extreme equivalents, and take the mean of them, rejecting all decimals which follow the first doubtful figure. Thus the two last decimals in his equivalent of lead are useless; since the experiments of Berzelius leave it doubtful whether the equivalent of lead may not fall short of 103·55 instead of exceeding that number. This doubt respecting lead again operates on the equivalents of nitrogen and sulphur; so that it is doubtful if the equivalents of these elements may not be smaller instead of greater than 14·16 and 16·09.

With regard to the numbers employed by British chemists, it is apparent that they are in many instances inconsistent with experiment. Numbers asserted to be correct to a minute fraction of a unit, are found in error to the extent of a unit and a half, or two entire units: the equivalent of silver, for instance, instead of being 110, is exactly or nearly 108; and the equivalent of barium has been reduced by Dr. Thomson himself from 70 to 68. The atomic weights

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[*] Poggendorff's Annalen, xxi. 614.

of chlorine and lead are likewise incorrect; and thus are found to be erroneous four quantities which have been employed as elements in calculating the equivalents of nearly all the other elementary substances. Under such circumstances, 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. I grant most willingly, that a system of whole numbers, considered as moderate approximations, may, with advantage, be retained for the use of medical men, students, and manufacturers; but as the strict representative of scientific truth, applicable to all the purposes of science, this hypothesis is at present untenable. Let me not however be misunderstood: I mean simply to affirm that the experiments by which it has been attempted to prove the truth of this hypothesis are inaccurate: I may go further, and declare it to be not only unsupported by evidence, but to be at variance with the most exact analytic researches which have been conducted. I deny not that some simple relation subsists among atomic weights, and that their ratios may possibly be expressed by some simple series of numbers; but at present no one has assigned any physical cause for the existence of such a relation; no such relation has hitherto been discovered; nor, as appears to me, has analytic chemistry attained that degree of perfection which can justify any one in finally asserting or denying its existence.