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THE
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- I. *An Attempt to determine the definite and simple Proportions, in which the constituent Parts of unorganic Substances are united with each other.* By JACOB BERZELIUS, Professor of Medicine and Pharmacy, and M.R.A. Stockholm.

[From GILBERT's Journal, 1811, iii. . . . Translated from a copy corrected by the Author expressly for this Work.]

PART FIRST.

MR. BERTHOLLET, one of the most celebrated chemists of our times, has endeavoured to demonstrate, in his ingenious researches respecting the laws of chemical affinities, that elementary substances may unite with each other in an infinite number of progressive proportions. Mr. Proust, however, another great master of the science, has shown, in opposition to him, that no such infinite variety of progressions is to be found in nature: but that all compound and precisely characterized bodies exhibit only a single and invariable proportion between their component parts; and that when a protoxide, for example, is converted by an additional portion of one of its component parts, that is of oxygen, into an oxide, this happens *per saltum*, proceeding at once to another precisely determined proportion, so that any continued series of combinations between these limits is out of the question. The truth of Proust's remark cannot have escaped any experienced chemist: but it has not hitherto been ascertained whether these distinct steps or stages of combination follow one and the same law for substances of all kinds, or whether the proportions are indeterminate, and different for different

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substances. The experiments, which I shall here relate, will prove that certain fixed laws prevail in all such cases.

I have been led to this investigation by attempting to deduce from calculation the quantity of oxygen contained in ammonia; on this occasion I discovered that the quantity of any base, by which a certain quantity of the muriatic acid is saturated, contains always the same quantity of oxygen: although in reality the merit of this discovery is due to Richter, who has endeavoured to demonstrate the principle, in the sixth part of his Essays, by some well imagined, though not fully satisfactory experiments, which have led him to adopt a series of numbers agreeing tolerably well with each other, but by no means perfectly accurate. The same law was observable in the sulphates, when Bucholz's analysis of the sulphate of baryta was made the basis of the calculation. There was however some disagreement in the two series; nor were the results consistent with other experiments; and it was necessary to take for granted the truth of the analysis of the muriate of silver instituted by Bucholz and Rose. I also found that, in the submuriates of lead and copper, the acid is combined with four times as much of the base as in the neutral salts.

I was in hopes of being able to discover the general principle of these remarkable relations by a correct investigation of the combinations of a variety of other similar substances. In the mean time I received a copy of Nicholson's Journal for November 1808, which contained an account of Wollaston's experiments on acid salts or supersalts, which had been suggested by the hypothesis of Dalton, that *when bodies are capable of being combined in different proportions, these proportions may always be expressed by multiplying the weight of one of the bodies by 1, 2, 3, 4, and so forth*: and Wollaston's experiments seemed to confirm the hypothesis. This view of the combinations of bodies appeared capable of illustrating so greatly the doctrine of affinity, that the confirmation of Dalton's hypothesis seemed to be the greatest step that chemistry, as a science, would have made during the whole time of its existence. On what experiments Dalton had founded his proposition, and in what manner he had extended its application, I am wholly ignorant; I cannot therefore determine whether my experiments simply confirm this hypothesis in its whole extent, or whether they have any tendency to modify it in any of its parts.

It will be proved by the following experiments, that *when two bodies, A and B, combine with each other in different*

ferent proportions, their respective quantities are always indicated by some of these simple expressions: 1 A with 1 B, the minimum, 1 A with $1\frac{1}{2}$ B, or perhaps rather 2 A with 3 B, 1 A with 2 B, and 1 A with 4 B. But there is no example in my experiments of the proportion 1 A with 3 B.

It will further be shown, that *when two bodies, A and B, have both affinities with two others, C and D, the quantities of C and D which are saturated by A, are precisely in the same proportion as the quantities which are saturated by B.* Thus, since 100 parts of lead are capable of combining in the first degree with 15.6 of sulphur and 7.8 of oxygen, and 100 parts of iron, according to the analysis which will hereafter be related, combine in the first degree with 58.8 of sulphur, the composition of the protoxide of iron may be computed by the simple proportion $15.6 : 7.8 = 58.8 : 29.4$, so that 100 parts of iron require to be combined with 29.4 of oxygen. This is confirmed by the experiments which I am about to communicate, and all binary combinations may be determined in the same manner. It has been ably demonstrated by Richter, that a similar principle is applicable to the combinations of salts.

It is obvious that the result of these calculations, supposing them to be well founded, must be susceptible of much greater accuracy and certainty than the common analysis. I have endeavoured to give the greatest possible precision to the analyses which I shall here relate, and I have repeated the most important of them more than once, before I allowed myself to depend on them. These are certainly free from errors of more than one or two parts in a thousand, and the others are within at most one half per cent. of the truth, but still only accurate enough to give approximations in computation. Perhaps we shall never succeed in analysing substances so accurately, as to obtain results agreeing with the proportions of the component parts to the last place of decimals: on the other hand, it will not be impossible, when we have a number of very accurate analyses, to correct them so by calculation, that all the elements of the computation of a combination may afford precisely the same result.

I shall arrange my experiments in the order which seems most convenient for the illustration of the subject, and I shall totally refrain from all theorizing. How far the results of the experiments confirm the theory, will be obvious without particular comment, and the ideas to which they lead

will naturally occur to every attentive reader without my assistance.

I. LEAD AND OXYGEN.

Lead, as is well known, affords three oxides. In order to ascertain the proportion of oxygen contained in them, I employed lead which was obtained by the reduction of the crystallized nitrate, and which was consequently free from any mixture of copper or silver.

A. *Yellow Oxide of Lead.*

1.) Ten grammes of lead were dissolved in pure nitric acid, and in order to avoid loss, the process was performed in a flask or receiver of glass held in an inclined position. The solution was poured into a weighed dish of platina, carefully evaporated, and exposed to a red heat. It afforded 10.77 grammes of oxide.

2.) The experiment was repeated, but the evaporation and ignition were performed in the same vessel which served for the solution. The result was 10.775 grammes of oxide of lead.

3.) In a third experiment a flask with a long neck was employed. When the salt began to be decomposed, a small quantity of a mealy sublimate attached itself for an instant to the neck of the vessel, and the vapours had not the smell of a perfectly pure nitric acid. When the flask had been heated throughout its whole length, the weight of the oxidated lead amounted to 10.78 grammes, or a little more than in the former experiments; and at the same time an appearance had taken place in this experiment, which showed that a small portion of the oxide of lead was carried off with the vapour of the acid which was expelled.

4.) Ten grammes of lead were dissolved in nitric acid, and precipitated by carbonated ammonia: the precipitate was placed on a weighed filter and well washed. It amounted to 12.9025 grammes of carbonated lead. Of this 12.77 grammes were ignited in a dish of platina; the residuum was 10.64 gr. of yellow oxide of lead, giving 10.75 for the whole quantity; so that 100 parts of lead had taken up 10.75 of oxygen. I conceived a suspicion that the carbonated ammonia might not have thrown down the whole quantity of lead; I therefore passed sulphurated hydrogen through the liquor of precipitation, and through the water with which the precipitate had been washed; but they were not rendered turbid by it in the slightest degree.

5.) The

5.) The experiment was repeated with 8 grammes of lead, which afforded 10·32 of carbonate and 8·8 of yellow oxide of lead; so that 100 parts of lead had again taken up $7\frac{1}{2}$ of oxygen.

Bucholz obtained from 300 grains of lead, which were dissolved in nitric acid, and precipitated by carbonated alkali, 320 grains of yellow oxide of lead; besides $4\frac{1}{2}$ grains of carbonated lead, which remained on the filter. This last is taken by Bucholz, as equivalent to 4 grains of the yellow oxide: this however is an error; the carbonate of lead loses $\frac{1}{3}$ of its weight, not $\frac{1}{2}$ only, by ignition; for 10 grammes of pure carbonate of lead, dried in a strong heat, afforded me, in three different experiments, 8·35 gr. of yellow oxide, so that we must allow only $3\frac{3}{4}$ grains for the $4\frac{1}{2}$, and the lead in Bucholz's experiment cannot have taken up more than 7·92 per cent. of oxygen.

From these experiments I think myself authorised to conclude, that those are the most accurate which give the proportion of oxygen from 7·75 to 7·8 for 100 of lead. Consequently the yellow oxide or protoxide of lead consists of

| | | | |
|--------|---------|----|-------|
| Lead | 92·764 | or | 100·0 |
| Oxygen | 7·236 | | 7·8 |
| | <hr/> | | <hr/> |
| | 100·000 | | 107·8 |

B. Red Oxide of Lead. Red Lead.

Red lead, as it occurs in commerce, I have found contaminated with sulphate and submuriate of lead, oxide of copper, and silica: so that little dependence can be placed on its analysis. It also contains much of the yellow oxide, which gives it a brighter colour than properly belongs to lead in this stage of oxidation.

In order to get rid of the yellow oxide, I digested some levigated red lead with weak distilled vinegar, at a temperature of 68° , as long as the vinegar continued to saturate itself: by these means the yellow oxide was dissolved, while the red remained unaltered, the colour only becoming deeper. After washing and drying in a very strong heat, 10 grammes of this red lead were ignited in a weighed platina dish; they lost ·29 gr. The oxide, which had become yellow, was now dissolved in vinegar; the sulphate of lead and silica which were left in this process, weighed when ignited ·135 gr. To the solution in vinegar nitrate of silver was added, and ·01 gr. of muriate of silver was precipitated, which answers to ·03 gr. of submuriate of lead; so that in the whole there was ·165 of foreign matter. Consequently

A 4

9·835 gr.

9·835 gr. of red lead had afforded ·29 of oxygen and 9·543 of yellow oxide, or 8·855 of lead, which had been united with ·98 of oxygen. Now $8·855 : ·98 = 100 : 11·07$; consequently 100 parts of lead, in becoming red lead, take up 11·07 of oxygen, and this oxide consists of 90 parts of lead and 10 of oxygen.

C. Brown Oxide of Lead.

It is well known that red lead, digested with nitric acid, affords a brown oxide of lead. While the nitric acid dissolves the yellow oxide and reduces a part of the red to yellow, it leaves the brown oxide undissolved, together with a quantity of impurities, especially sulphate of lead and silica.

Five grammes of brown oxide of lead, freed by washing from all the nitrate which had adhered to it, and dried in a sand-bath, with a heat capable of melting tin, were ignited in a weighed dish of platina, and lost ·325 gr. of oxygen. The remaining 4·675 gr. of yellow oxide, dissolved in vinegar, left behind some sulphate of lead and silica, which when ignited weighed together ·13 gr. The remaining 4·545 gr. of yellow oxide contain ·33 gr. of oxygen, a quantity differing only by ·005 gr. from that which the brown oxide had lost by ignition. Consequently 100 parts of lead, in order to be converted into brown oxide, require twice as much oxygen as is contained in the yellow oxide, and the brown oxide consists of

| | | |
|------|--------|-------|
| Lead | 86·51 | 100·0 |
| | 13·49 | 15·6 |
| | <hr/> | <hr/> |
| | 100·00 | 115·6 |

It seems to follow as the result of these experiments, that lead, in its three different degrees of oxidation, takes up oxygen in quantities which are related in the proportions of 1, $1\frac{1}{2}$, and 2.

[To be continued.]

II. *Derivation of one of the Equations in LAPLACE'S "Mécanique Céleste."*

To Mr. Tilloch.

DEAR SIR, THE accompanying paper I had from my particular friend and successor in the mathematical school of Dumfries, Mr. Thomas White. That school I established about 40 years ago, and Mr. White has taught it with