



## XXIV. Observations on the doctrines of definite proportions in chemical affinity

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An example or two will make this clear. Let the cube number whose root is required be 804357. Here the first figure of the root will be 3, and the root of the greatest cube contained in 804 is 9. Hence the root required is 93.

Again. Required the cube root of 74088. Here 2 is the first figure of the root, and the root of the greatest cube contained in 74 is 4; hence 42 is the root required.

If only the figure of the unit, the two first figures, and the number of places be given, as stated in the question, the operation will be precisely the same. For by taking the example given in the question, the first figure of the root is 6; and as the number consists of 6 places, it remains only to find the root of the greatest cube number contained in 430, which is 7. Hence the root is 76. It may be proper however to remark, that this mode of stating the question fails when the given cube number terminates with a cypher.

Concerning the performing this "instantly and without any aid of writing," I beg to observe, that when I first discovered the principle, I explained it to two or three young gentlemen, pupils of mine, about twelve years of age, and who, after practising it for the short time of half an hour on a slate, would tell without the aid of writing, the root of any cube number under a million, instantly, and without the smallest hesitation.

The method applies also to any cube number above a million, when it terminates in a cypher; but I have not been able to extend it to cube numbers in general. I make no doubt but that with a little pains many other arithmetical operations might be simplified; and it would perhaps explain in a way not the most unsatisfactory, the truly astonishing powers of the "wonderful American boy." I am, &c.

GEORGE HARVEY.

*To Messrs. Nicholson and Tilloch.*

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XXIV. *Observations on the Doctrines of definite Proportions in Chemical Affinity* By WILLIAM CRANE, Jun. M.D. of Boston, Lincolnshire\*.

It is often a pleasing task to view the progressive improvement that is attendant upon different departments of science; in doing which we sometimes meet with hypotheses that were considered at first as crude, ridiculous, and soon almost forgotten, again revived, more clearly illustrated, and not unfrequently advanced as entirely new. Among many others that have been proposed in the science of chemistry, that of bodies uniting in definite proportions to form chemical compounds holds a distinguished place.

\* Communicated by the author.

Mr. Higgins, in his Comparative View of the Phlogistic and Anti-phlogistic Theories, conceiving that bodies were composed of minute atoms, was led, from the well-known fact that oxygen and hydrogen gases united in the proportion of 1 to 2 in volume to form water, and as they unite in no other proportion, to consider them as uniting atom to atom. "We must suppose," he observes, "that they contain an equal number of divisions, and that the difference of their specific gravity depends chiefly on the size of their ultimate particles; or we must suppose that the ultimate particles of light inflammable air require 2 or 3 or more of dephlogisticated air to saturate them." The latter, he infers, is not the case, from its being impossible to form such an intermediate combination as can be effected in the union of sulphur and oxygen. From this also he concludes, that oxygen and hydrogen "are incapable of uniting to a third particle of either of their constituent principles." Sulphuric acid, according to him, is formed of 1 particle of sulphur and 2 of oxygen, and sulphureous acid by 1 of sulphur and 1 of oxygen.

These speculations, owing to the imperfect state of chemical analysis, were overlooked and rejected by succeeding chemists, and little or no notice taken of them until Mr. Dalton, in a work displaying the vast powers of an enlightened mind, aided by industrious research, repropounded this doctrine, and again turned the attention of chemists to this important subject; and it appears to me, from perusing Mr. Dalton's new System of Chemical Philosophy, that he is unacquainted with the writings of Mr. Higgins on this subject. The former has, in the work just mentioned, stated that chemical attraction is guided by determinate laws; that bodies uniting to each other in one proportion only, unite atom to atom, or those which combine in various proportions form binary, ternary, &c. combinations, one atom of the one element being united to 1, 2, 3, &c. atoms of another. Examples are found in the union of oxygen and hydrogen, oxygen and azote, &c. one atom of the one uniting to one or more atoms of the other; according to some fixed mathematical relation, which Mr. Dalton apparently considers to be in arithmetical progression. In this view of affinity, it is of importance to determine the number of elementary atoms that enter into the formation of a compound atom. Hence, should this supposition be found correct, the errors arising from chemical analysis may be regulated by the aid of mathematical calculation. The two substances that have claimed particular attention, by which this may be accomplished, are water and ammonia, for the elements of these have as yet been found to unite in one proportion only.

Mr. Murray, in his Chemistry, has observed, that the facility with which the numbers can be assumed is one of the means by which we may be deceived.

Dr.

Dr. Thomson, in his System of Chemistry, gave an outline of Mr. Dalton's theory, before the latter had himself made it public, and in his paper upon the oxalic acid in the Philosophical Transactions for 1807 has shown a very great coincidence in the composition of this acid, by calculation, with the result of actual analysis. In the 4th section of this paper he states that "it has been ascertained by decisive experiment, that elementary bodies always enter into combinations in determinate proportions, which may be represented by numbers;" and he finds an atom of oxygen to be 6, if an atom of hydrogen be estimated as 1. The Doctor has taken this estimate by supposing one atom of oxygen to unite to one of hydrogen, to form water; estimating the weight of hydrogen to be  $14\frac{1}{3}$  and oxygen to be  $85\frac{2}{3}$ , to form 100 parts of water: hence an atom of hydrogen being to one of oxygen in the same ratio, it gives when reduced 1 to 6.48, and the Doctor rejected the decimals. Mr. Dalton takes his estimate from the proportion given by Humboldt and Gay-Lussac. It appears from their experiments to be 87.4 of oxygen to 12.6 of hydrogen; and the number representing oxygen will be 6.96, which approximates very nearly to 7, the number chosen by Mr. Dalton.

Sir H. Davy estimates the specific gravity of hydrogen to oxygen as 1 to 15; and as it takes 2 measures of hydrogen to 1 of oxygen in the formation of water, the ratio of the hydrogen to oxygen is as 2 to 15\*; "and it may be regarded as composed of 2 proportions of hydrogen and 1 of oxygen, and the number representing hydrogen will be 1, and that representing oxygen 15." This value is not taken by considering the number of atoms in the gases, a doctrine truly hypothetical, but from the proportions in which they unite, and their specific gravity. In considering the doctrine of proportion, as Sir H. Davy has observed, we certainly have no reason to suppose bodies composed of atoms that are indivisible uniting one to one, &c. In the present state of our knowledge this hypothesis of atoms cannot with propriety be admitted, as we have no evidence upon which we can be certain of the weight or number of atoms in any compound. "Our numerical expressions," as the author last quoted justly says, "ought only to relate to the result of our experiments."

It is not a little perplexing to observe Mr. Dalton, in his work, found his whole calculation upon the combination of oxygen and hydrogen as uniting atom to atom to form water; and in his chapter upon the combination of these gases, to find him declare that "after all it must be allowed to be possible that water may be a *ternary compound*." This conclusion appears in a great measure to be drawn from his experiments upon muriatic and

\* Elements of Chemical Philosophy, p. 112.

fluoric acids, in which he concluded they were formed by the union of oxygen and hydrogen in different proportions. Later discoveries have proved this not to be the case. For oxymuriatic acid, now called chlorine, appears to be the basis of the muriatic acid; and fluoric acid, from the experiments of Davy, Gay-Lussac and Thenard, also has a peculiar base.

Notwithstanding the theory of atoms is so very hypothetical, it is applicable to calculation, as the numbers are relative, and taken from a fixed ratio. Therefore, if we take the original proposition that water be composed of equal atoms of these gases, I am inclined to think 6.96 as very near the true number for oxygen. I am not fond of rejecting decimals, as these, when there is a combination consisting of some high multiple, will lead to considerable error in the calculation, or when the substance under examination consists of many parts.

Dr. Thomson in his paper on oxalic acid, when calculating the composition of this acid, takes oxygen at 6, and hydrogen at 1, and carbon, with Mr. Dalton, at 4.3; and he finds from experiment the composition of oxalic acid to be,

Oxygen ..	64.69, and by calculation	Oxygen ..	61
Carbon ..	31.78 .. ..	Carbon ..	34
Hydrogen	3.53 .. ..	Hydrogen	5
<hr/>		<hr/>	
100.00		100	

If the number representing oxygen be taken, as I have above mentioned, 6.96, calculation gives

Oxygen .....	64.24	which comes ex-
Carbon .....	31.15	tremely near.
Hydrogen .....	4.61	
<hr/>		
100.00		

The numbers given by Sir H. Davy, being reduced to Mr. Dalton's views, and applying them as above, appear to be too high. After Dr. Thomson, we find that Dr. Wollaston also read a paper to the Royal Society, giving an account of some experiments he had made upon sub-acid and super-acid salts. These he considers as particular examples of Mr. Dalton's more general rule, which he states thus: "that in all cases the simple elements of bodies are disposed to unite atom to atom singly; or, if either is in excess, it exceeds by a ratio to be expressed by some simple multiple of the number of its atoms."

When examining the oxalates, he found the super-oxalate to contain twice the quantity of acid the neutral salt contains. Hence it is probable that it unites in the proportion of 1 of potassa to 1 of acid, and 2 of acid to 1 of potassa: therefore the next combination, if it be formed, ought to consist of 3 of acid to 1 of alkali. To determine this, the Doctor took 400 grains of potassa and neutralized it with 30 of acid; to this he added 60 grains  
more

more of acid ; so there were 2 parts of potassa 24 grains each, and six equivalent parts of acid 15 grains each ; which ought, as above stated, to form a salt of 3 of acid to 1 of alkali. But upon crystallization he found 2 salts, the one a binoxalate, the other a quadroxalate, or one of alkali to 4 of acid.

To make this answer to the theory of Dalton, the Doctor supposes the neutral salt to consist of 2 of alkali to 1 of acid, and the next 2 to 2, and the third 1 to 2, or 2 of alkali to 4 of acid. This is altogether hypothetical ; and, as Dr. Wollaston observes, it is far from satisfactory that the alkali should be in excess in the neutral salt.

Although this appears against Mr. Dalton's theory, it is equally so to the law of Berthollet, that the combinations of bodies are as their relative attractions and acting masses : for, Why in that case are the salts above mentioned formed ? The alkali ought to be diffused equally, and a salt consisting of 3 to 1 obtained.

Dr. Wollaston thinks it is probable that other ratios will be found, arising from the shape and polarity of the atoms, than the simple arithmetical.

Gay-Lussac has attempted to form a theory departing from the strict principles of Berthollet's views of affinity and those of Dalton. He thinks chemical affinity may be indefinitely exerted amongst the particles of matter, and compounds may be formed of variable proportions ; but that insolubility, cohesion, and elasticity have a tendency to produce fixed combinations ; and also that chemical action takes place with energy when the elements are in simple ratios, or some multiple of these ratios, by which compounds are produced that can be easily insulated.

By this means he endeavours to explain the phenomena attending chemical affinity ; that bodies can unite in determinate proportions, and that under certain circumstances they unite according to the quantity of attracting matter, and form compounds of variable relations : and a view of this kind has been in some measure adopted by Berthollet. With respect to the combinations of the gases, Gay-Lussac has observed two laws. 1. That they combine in proportions having simple ratios according to their volume. 2. That gases by combination appear to suffer a contraction in volume in a simple ratio to the gas added. After having stated many examples of his first law, he also adds, that between the elements of the first combination there is no simple ratio ; but this takes place in the second combination, when the new proportion will be a multiple of that first added. This, as Mr. Murray observes in his *System of Chemistry*, from which I have taken this outline of Gay-Lussac's theory, distinguishes his from that proposed by Dalton. To these speculations of Gay-Lussac, Mr. Dalton has replied in the Ap-

pendix to the Second Part of his work, appealing to his own experiments and those of the most celebrated chemists, that gases do not unite in measures proportionate to their volume.

After having cited particular examples that many of them do not unite in volume according to any determinate proportion, he concludes, "that gases in *no* instance combine in equal or exact measure." This, Mr. Murray thinks, might be perhaps properly extended to the whole doctrine of definite proportions.

Sir H. Davy, in his *Elements of Chemical Philosophy*, advances an immense number of proofs that the theory of definite proportions is not founded upon hypothetical reasoning. He, as is already observed, rejects the doctrine of atoms, and founds his calculations on the result of actual experiment. By this, one of the very great objections to Mr. Higgins's and Mr. Dalton's theory is removed; namely, that substances uniting in one proportion only form a binary compound, for we have no grounds upon which we can form such an opinion in the language of Mr. Dalton; it is merely an assumption. He supports, contrary to what Mr. Dalton has said, the theory advanced by Gay-Lussac, respecting the union of gases; which he beautifully illustrates by the combinations that are formed by azote and oxygen, carbon and oxygen, &c. And Mr. J. Davy, in his paper published in the *Philosophical Transactions*, On the gaseous Compounds of Carbonic Oxide and Chlorine, has given some very decisive examples. He observes, "the proportions in which bodies unite appear to be determined by fixed laws, which are exemplified in a variety of instances, and particularly in the present compounds. Oxygen combines with twice its volume of hydrogen, and twice its volume of carbonic oxide, to form water and carbonic acid; and with double its volume of chlorine to form euehlorine; and chlorine reciprocally requires its own volume of hydrogen and its own volume of carbonic oxide to form muriatic acid and the new gas."

Sir H. Davy in his work has noticed several of the experiments upon which Berthollet founded his views of affinity, and has pointed out the source of some errors. According to Berthollet's views, precipitates could not be thrown down in a state of purity, but must retain a portion of the substance with which the precipitate was previously combined: of this we have many examples to the contrary, as when one metal in solution is precipitated by another; and in the precipitation of magnesia, &c.

Sir H. Davy also observes, "that there is no difficulty in reconciling the doctrine of proportions with the influence of quantity. None of the experiments of M. Berthollet can be considered as strictly contrary to the doctrine, and some of the most important results of this sagacious chemist afford its confirmation."

From the above quotations and observations, I think it will clearly

clearly appear that the doctrine of Messrs. Higgins and Dalton with regard to atoms is truly hypothetical, and cannot with propriety be at present admitted: objections to this theory have also been pointed out by Dr. Bostock in Nicholson's Journal. The views I am most inclined to adopt are those of Sir H. Davy, as in these we are guided by the result of experiment and fact. The more accurately our researches are made, the more forcibly is the doctrine of definite proportions demonstrated. The researches of Mr. J. Davy on the combinations of different metals and chlorine, published in the Philosophical Transactions for 1812, and the late interesting publication of Berzelius, sufficiently prove the truth of what is above stated: although not standing the test of a rigorous mathematical examination, they are sufficiently near, considering that chemical analysis is still imperfect, to point out this grand law. Objections may undoubtedly still be urged against it, and that of solution has been considered by some as the most forcible; since, in this, bodies within certain limits appear to unite in any proportion. But surely there is some difference between dissolution and combination: in the former we find merely the cohesion of the compound aggregates amongst each other disunited, and the particles of the compound diffused throughout the fluid: in the latter, a decomposition takes place amongst the elements of which a compound is formed, it assumes entirely new properties; and it is here we are to look for the determinate action of affinity. If it were not guided by such a law, our results would always be showing different productions, and compounds consisting of the some proportion of elements would scarcely ever be obtained.

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XXV. *Notes and Observations on the remaining part of the Seventh Chapter of Mr. ROBERT BAKEWELL'S "Introduction to Geology;"—embracing incidentally, several new Points of Geological Investigation and Theory. By Mr. JOHN FAREY Sen., Mineral Surveyor.*

[Continued from p. 34.]

*Notes, &c.*

P. 182, l. 6, from the ocean†.—† The great south-eastern Denudation of England ¶, probably includes the Basin of Paris in its upper eastern edge, P. M. xxxv. p. 130 and 134, notes; but

¶ The acknowledgement of this characteristic phenomenon of the counties of Kent, Sussex, Surrey, and the eastern part of Hampshire (the first Denudated tract that was well ascertained probably) seems with difficulty or reluctance made, by the Wernerian School: a learned Doctor, when lately