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## XXVIII. On the Atomic Theory

## William Higgins Esq.

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## XXVIII. On the Atomic Theory. By WILLIAM HIGGINS, Esq.

## To Mr. Tilloch.

SIR, -- I BEG leave to transmit to you the following observations, which I request you will insert in your Magazine. The first part relates to the article *Atomic Theory*, published in Dr. Rees's new Cyclopædia, vol. xxxv. part 2. The author I know, for it is impossible to mistake his prejudiced style of writing.

The writer begins by giving a definition of the Atomic Theory of Chemistry. "It is the means of explaining the composition and decomposition of chemical bodies, by considering their ultimate atoms<sup>\*</sup> or particles as peculiar and distinct elementary solids, never changing in their figure, weight or volume, under any circumstance."

The definition is very fair : and I will say with confidence that I was the inventor of this theory, and the first that applied it in the manner above described ; and I defy any person to produce any thing to the contrary,—I mean any person that will step forward without confounding dates and facts, as has been the case repeatedly on the subject of the Atomic Theory.

The writer proceeds in continuation, on the supposition of the infinite and definite proportions in which elementary matter might, or might not, combine. This I must pass over, as it has nothing to do with the present discussion.

"Philosophers," says he, "were always satisfied to consider this fact of the limitation of the proportions of bodies, as one of the hidden secrets of nature, as difficult to conceive as the nature of the attraction by which their elements were held together. Berthollet appears to have been the first to attempt this arduous task, in his ingenious work entitled *Chemical Statics.*"

As Count Berthollet's work does not materially relate to my Atomic Theory, and as he had written some years after me, I shall make no comments on this part of the subject: I will only say that my *Comparative View* should have, in the history, a precedency of the *Chemical Statics*, where this arduous task, as he calls it, was first attempted with perfect success.

"Chemists have from the earliest times been acquainted with those points which we call mutual saturation, and have been long familiar with those limited augmentations of their proportions called by some doses, and by others particles."

The ancient chemists were well aware that one body required a given portion of another body to saturate it so as to form a neutral compound; but their knowledge went no further,—they

\* He should leave out the word *atom*, as being a compound. Vol. 51. No.239. March 1818. L had had no conception of the laws that regulated the limitation, because they were not aware that bodies united particle to particle and atom to atom in certain but limited proportions. In short, the cause of this law was unknown until I published my Comparative View.

The writer tells us that the true nature of metallic oxides was not known until Lavoisier's time :---How could it be known, when their oxidation was solely attributed to a loss of their phlogiston? But the first idea of metals uniting to different doses of oxygen, like sulphur, charcoal and azote, will be found in my *Comparative View*.

"Although chemists have frequently used a language which appeared to show their acquaintance with the real cause of the definite proportions; such as one compound being formed by one proportion, dose or particle, of one of its elements; and another with two proportions, doses or particles\*: on the other hand, we find expressions which would favour the idea of indefinite proportions; such as bodies losing a small portion of their oxygen, or absorbing a little oxygen from the atmosphere." The drift of the latter part of this passage will appear presently.

"The most decided language used in any chemical work before the discoveries of Mr. John Dalton †, giving any idea that the doses are limited by distinct atoms, will be found in a work by Mr. Higgins, entitled 'A Comparative View of the Phlogistic and Antiphlogistic Theories." This work was written for the express purpose of combating the phlogistic theory, and principally in answer to Kirwan's Treatise of Phlogiston.

" In order to show the contradictions and absurdities of the phlogistic doctrine, which under the name of phlogiston confounded a number of bodies which were very different, he exhibited by diagrams a number of chemical operations, in which he supposed the elementary bodies concerned to be ultimate particles, and their immediate compounds molecules. He in the same diagrams also used numbers, which he supposed to be estimates of the strength of affinity of the combining particles. By this means he very successfully showed many of the inconsistencies which must be admitted to explain the phænomena on the phlogistic theory. In this mode of proceeding, however, the numbers expressing the relative attractions served his purpose much more than the consideration of the proportions being caused by distinct atoms; and the language which would induce the belief that he had such a conception of the nature of elementary matter occurs only in a very few parts of his work."

\* No such language was used until I had written.

† It would puzzle the first philosophers of Europe to discover any thing new in Mr.Dalton's work, except his errors which I have repeatedly pointed out. The The numbers alone would avail nothing, if they had not been coupled with the proportions of particles which constituted different compounds, and vice vers $\hat{a}$ ; and the language expressive of those ideas runs uniformly and conspicuously throughout my whole work.

"After concluding that it is unnecessary to admit the existence of the imaginary substance, phlogiston, in sulphur, he concludes, in page 36, that sulphurous acid is compounded of one ultimate particle of sulphur with one of oxygen, and that sulphuric acid consists of one of sulphur and two of oxygen.

" In the same page he also observes, that water is formed of one ultimate particle of water\* united to one of oxygen."

The author next quotes my statement of the constituents of sulphuretted hydrogen, and the porportions which their respective particles bear to each other, and then passes to my estimate of the proportions of the particles of azote and oxygen in nitrous oxide, nitrous air, red nitrous acid, straw-coloured nitrous acid, and in the nitric acid.

"These facts," continues he, "are certainly very remarkable, as they agree with the conclusions in the present time, and give a strong proof of Mr. Higgins's genius at the time he wrote.

"He does not, however, lay any stress upon these remarks, and was not probably aware that they would be confirmed by future research." I was perfectly satisfied that I was right, and that my demonstrations would bear the test of time and investigation  $\dagger$ ; and the best stress I could set upon them was, to lay them before the public. But he goes on: "We are induced to think so from the manner in which he expresses himself in other parts of his work, in which he frequently speaks of the absorption of small portions of oxygen, and of bodies having a small portion of oxygen more than they can retain."

These remarks do not in the smallest degree invalidate the principles which I advanced. We know that distilled water absorbs oxygen from the atmosphere, that all the sulphites gradually absorb oxygen from the atmosphere, so as, in time, to become sulphates. And many substances contain more oxygen than they can well retain;—instance, nitric acid, euchlorine, oxymuriate of potash, and the oxides of gold and silver, particularly the latter.

"This vague manner of speaking, and others which we do not immediately recollect, is sufficient to show that Mr. Higgins had no fixed notions of the cause of definite proportions; and the language in which he has used ultimate particles and molecules,

<sup>\*</sup> The author made a mistake; read a particle of hydrogen instead of a particle o water.

<sup>†</sup> See preface to my Comparative View.

was employed rather with a view to illustrate his examples, than to broach any new theory to explain definite proportions. Indeed it would have been inconsistent to have treated two subjects so very different in their objects, in the same pages,"

I will now, before I proceed any further with the author of this article, remark that I made no use of vague or equivocal language, and that I entertained fixed notions of the laws of definite proportions, which are fully demonstrated throughout the whole of my *Comparative View*. It is true I gave no name to the novel mode which I adopted for the purpose of my research, --but what is a name but a mere shadow in comparison to the matter itself? Lavoisier never gave a name to his doctrine. Kirwan was the first that gave it the name of the antiphlogistic theory; and I will say that it was not inconsistent to trace the errors of the phlogistians in the same page, and even in the same paragraph, by means of the laws of definite proportions; and it was in consequence of that close investigation that the Atomic Theory started up in my mind; otherwise, in all probability, it would have still remained unknown.

The author tells us in another part of this article, that the reviewer of this work (the Comparative View) in the Analytical Review soon after it was published, took no notice of my diagrams or particles, although he gives me the highest praise for the able manner in which I refuted the doctrine of phlogiston. This he adduces as a proof that there was nothing striking in what I advanced on the theory of definite proportions. The Reviewer, it is true, only observed that " my facts and mode of reasoning were original and striking." What more could be expected at a time when there was no fixed theory, and when the science was almost in a chaotic state? It was impossible that such novel view should all at once be adopted even in the most advanced state or the science of chemistry.

My diagrams were taken notice of in the *Critical Review*, at the time I had written, and the remarks made on them show the ignorance of those days; for they only observed that they were the same with those of Dr. Black. And Dr. Thomson himself, after I published my Essay on the Atomic Theory, &c. mentioned in one of his Journals, (I forget in what number, for I have it not by me at present,) that there was nothing material in those diagrams of mine, for indeed that Dr. Black's were much more pretty than mine. What a scientific expression from a compiler of philosophy!

I scarcely need to tell the reader that Dr. Black's diagrams and mine bear no relation whatever to each other.

But the writer goes on. "It was not enough to know that compound bodies were formed of particles, to enable us to explain plain the cause of definite proportions; and we want not greater proof of this than the fact of the true cause not being known till twenty-eight years after Mr. Higgins had told us that one particle of sulphur and one of oxygen formed sulphurous acid, and that one to two formed sulphuric acid. These loose expressions were but a small step indeed towards the discovery of the Atomic Theory in its present form, which has placed chemistry on the same ground with that on which the discovery of the laws of gravity placed the science of astronomy."

The above paragraph is written with a great deal of disingenuity, and evidently could only flow from the pen of a prejudiced man. We could never be acquainted with the cause of definite proportion without first knowing that compounds consisted of elementary particles; and the proportions of those particles, the relative forces with which they unite in different compounds, and their relative weights :---all these constitute the Atomic Theory; and those important circumstances are unequivocally, not loosely, to be met with in my *Comparative View*. It was the pride of my life since I had written that work, to feel that " I placed chemistry on the same ground with that on which the discovery of the laws of attraction placed the science of astronomy."

The following quotation from the preface of my Essay on Bleaching, page 18, will show how confident I was that what I advanced in my Comparative View was perfectly just, viz. "I have connected the whole (the facts and phænomena then known) and reduced them to a system, and made use of demonstrations, which in my opinion are not to be invalidated or contradicted, until the order of natural things assume a different aspect."

The above Essay was published in the year 1799, many years before Dalton's work appeared.—But to return to our writer.

"We are inclined to believe that the first step towards this important discovery was given by Richter. He found in the double decomposition of salts, that the acid of one salt was always just sufficient to saturate the base of the other, and vice verså." So far as the decomposition takes place this holds good, but in other respects there are many exceptions.

"He also ascertained, that when one metal was precipitated by another, the oxygen of the precipitated metal was just what was required by the precipitating metal."

I wrote several years before Richter; and many of the chemists of the time at which I published, as well as myself, were acquainted with what this gentleman attributes to Richter\*. The ancients

\* The mutual saturation of saline bodies on interchanging acids and bases with each other; that is, double decomposition.

knew

knew as well as Richter, that in the gross, one quantity of alkali required a certain quantity of acid to saturate each other,—and what more can he attribute to Richter? It has nothing to do with the atomic theory and definite proportions of particles or atoms.

And as to what relates to metallie precipitations, he is wrong in many respects, as I have shown in my Comparative View, page 263, which the following extract will show: "Should the precipitant be unable to take up the whole of the oxygen of the precipitated metal, it falls down in the state of a semioxide. Thus lead and silver will precipitate gold from its solution of a dull purple colour, while copper and iron throw it down in its metallic state."

I now come to the most singular passage of all, as it exhibits the most glaring prejudice and ignorance that could flow from the mind of any man that could have any pretensions to science; it is as follows: "It is the means of drawing these inferences arising from the mutual fitness of those parts of bodies which combine, that constitutes the importance of the Atomic Theory; and it is for the establishment of this new principle that we are indebted to Mr. John Dalton. When Mr. Higgins can show from the data given in his work, that similar inferences could be drawn, he then will be entitled to share in the merit of the discovery of the Atomic Theory. We say share with him; for we are firmly convinced that Mr. Dalton had never read Mr. Higgins's book previous to the publication of his own work."

There is nothing new, as I said before, in these facts, they were known before I wrote my *Comparative View*; and the mutual fitness (which by the by is an odd expression) of some of them, for it does not extend to all saline bodies, was familiar to every experimental chemist, and Mr. Dalton has nothing to do with it; nor does it immediately relate to the Atomic Theory.

"When Higgins can show that similar inferences, &c."

I will adduce some facts which, according to the writer, will " entitle me to share in the Atomic Theory." In the section on the precipitation of metals by each other, page 260 Comparative View, will be found a diagram representing the principles on which one metal precipitates another. The precipitation of copper in its metallic state from its solution in sulphuric acid by iron, was adduced as an example. The diagram represents by means of numbers the relative forces of attraction of the different elements in a molecule of sulphate of copper, and also the influence of a particle of iron on each of those elementary princi-The play of affinities which enables ples united to the copper. the particle of iron to strip the particle of copper of the whole of its oxygen and volatile sulphurous acid, so as to leave it in its pure

pure metallic state, is minutely explained, and is highly interesting \*. There are two more diagrams, somewhat different from the former, representing the precipitation of mercury and silver in their metallic state, on the principles of what is also No such philosophy is to be found called the Atomic Theory. in Dalton's work; no, nothing is to be seen there but bombastical and erroneous imitations of my doctrine forced on the public by hirelings. The respectable editor of this useful work will, it is to be hoped, be careful in future who he employs. That the writer of this article should assert that Mr. Dalton never read my work previous to the publication of his own, is rather extraordinary; for no man can know what any other individual Dalton himself has never denied his reads or does not read. having read it—at least publicly. There is nothing else in this article that I had not taken notice of in my observations on the same subject in the Encyclopædia Britannica, and which was The writer tells us that Mr. Dalpublished in this Magazine. ton's book was published some time before chemists understood the true spirit of the Atomic Theory. I believe it is not perfectly understood at present, or else I should not have so much trouble to establish my claim. If Mr. Dalton's work was so difficult to be understood in the present day, surely it could not be wondered at, that the original should lie by unnoticed in a more obscure age of chemical philosophy.

On lately casting my eyes over Dr. Wollaston's paper on the Synoptical Scale of Chemical Equivalents, I observed some remarks on my theory, or, as he unjustly calls it, Dalton's theory.

The Doctor, after having given the opinion of different chemists on the relative quantities of acid united to a given quantity of alkaline and earthy bases, observes that, "It could not escape the penetration of M. Berthollet, that there exist numerous deviations from this law of neutralization, and cases of prevailing affinity dependent on a redundance of one or other ingredient in a mixture of salts. But he was not so happy in detecting the definite law, by which many at least of these deviations are governed. It has since been found, that when a base unites with a larger portion of acid than is sufficient to saturate it, the quantity combined is then an exact simple multiple of the former, thus exhibiting a new modification of the law of definite proportions rather than any exception to it.

"The first instance in which the same body was supposed to unite with different doses of another, in such proportions that one of these doses is a simple multiple of the other, was noticed

\* The diagram and explanation may be seen also in my Essay on the Atomic Theory, page 158.

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by Mr. Higgins, who conceived rather than actually observed to occur, certain successive degrees of oxidation of azote, and represented the series of its combinations with oxygen to be azote, one with two of oxygen making nitrous gas."

He continues to the end of the series of the combinations of those elements to nitric acid which limits their combination, and marks their definite proportions. But what the Doctor means by the expressions "conceived, rather than actually observed to occur," I do not perfectly understand. It is too ambiguous. If he means that it was not founded on facts, I cannot agree with him; for I have adduced a great many to confirm my positions, which may be found in different parts of my Comparative View, but particularly under the section Nitrous acid.

If he means that I accidentally stumbled on the idea, I have had a great many such stumbles throughout 280 miles (280 pages), and yet I have not once tumbled. Perhaps he means that I dreamed of the thing; if so, it must be a very happy and a very long and well-connected kind of a dream, such as seldom occurs.

"But," continues the Doctor, "though Mr.Higgins, in the instance of the union of hydrogen and oxygen, anticipated the law of bulks observed by M. Gay-Lussac, with respect to the union of gases, and in his conception of union, by ultimate particles, clearly preceded Mr.Dalton in his atomic views of chemical combination, he appears not to have taken much pains to ascertain the actual prevalence of that law of multiple proportions by which the atomic theory is best supported; and it is in fact to Mr. Dalton that we are indebted for the first correct observation of such an instance of a simple multiple in the union of nitrous gas with oxygen."

I have also shown the proportions in which carburetted hydrogen and oxygen united so as to produce water and carbonic acid gas, and that this gas contained two-thirds of oxygen and one-third charcoal \*. In short, I was acquainted with the proportions in which all the gases united in volumes ;----and it evidently appears throughout most parts of my work, that I have taken great pains to ascertain the actual prevalence of that law of multiple proportions by which the Atomic Theory is best supported; and that it is not in fact to Mr. Dalton that we are indebted for the first correct observation of such an instance of a simple multiple in the union of nitrous gas with oxygen. The Doctor could not bring forward a more unfortunate instance than the latter to support his friend, as I have fully proved upon a former occasion in the number of this Magazine for May last. I will now suffer the Doctor to go on.

" Chemists in general," says he, " however, appear to have

\* See pages 252-53 Comp. View.

been

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been by no means duly impressed with the importance of this observation of Mr. Dalton, till they were in possession of other facts observed by Dr. Thomson and myself, in a more tangible form, with regard to neutral and super-acid or sub-acid salts, &c." He here refers the reader to Phil. Trans. 1808, p. 74 and 96, to which we will now pass.

The paper now under our consideration is entitled, On Superacid and Sub-acid Salts. By William Hyde Wollaston, M.D. Sec. R.S. Read January 28, 1808.

"Dr. Thomson," says he, "has remarked, that oxalic acid unites to strontian as well as to potash in two different proportions; and the quantity of acid combined with each of these bases in their super-oxalates, is just double of that which is saturated by the same quantity of base in their neutral compounds."

The Doctor tells us that he observed the same law to prevail in various other instances of super-acid and sub-acid salts; and as he considered it general, it was his intention to pursue the subject, " with the hope of discovering the cause to which so regular a relation might be ascribed."

"But since the publication of Mr. Dalton's Theory of Chemical Combinations as explained and illustrated by Dr. Thomson, the inquiry which I had designed appears to be superfluous, as all the facts that I had observed, are but particular instances of the more general observations of Mr. Dalton—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."

In the foregoing paragraphs the Doctor to my great surprise, and indeed to the surprise of every honest and liberal-minded man, transfers over to Mr. Dalton those principles which are so clearly developed in my Comparative View, and which he himself was obliged to allow five years afterwards, as I have already shown in this paper.

But as the Doctor supposes that his intended experiments might throw additional light on the theory of Dalton, he is determined to go on with them. He commences with the subcarbonate of potash.

"*Experiment* 1. Sub-carbonate of potash recently prepared is one instance of an alkali having one-half the quantity of acid necessary for its saturation, as may thus be satisfactorily proved.

"Let two grains of fully saturated and well crystallized carbonate of potash be wrapped in a piece of thin paper, and passed up into an inverted tube filled with mercury, and let the gas be

It would have been more correct to have said particle to particle singly. extricated

extricated from it by a sufficient quantity of muriatic acid, so that the space it occupies may be marked upon the tube.

"Next let four grains of the same carbonate be exposed for a short time to a red heat, and it will be found to have parted with exactly half its 'gas; for the gas extricated from it in the same apparatus will be found to occupy exactly the same space, as the quantity before obtained from two grains of fully saturated carbonate\*.

"A similar experiment may be made with a saturated carbonate of soda, and with the same result; for this also becomes a true semi-carbonate by being exposed for a short time to a red heat."

There can be nothing novel in those observations of Dr. Wollaston. The same may be seen in my Comparative View, pages 40 and 41. In explaining a diagram representing an atom of sulphuric acid with its two particles of oxygen united to one particle of sulphur, with numbers expressive of the force of their union, I observed that if one of the particles of oxygen were removed, the other would become more strongly united; and when the second particle was again restored, the force of union would be diminished as the quantum of attraction of the particle of sulphur would be divided equally between them.—Here follows an extract in continuation of the above explanation  $\uparrow$ .

"This seems to be a general law: all bodies unite with greater force to half the quantity of those substances to which they have an affinity than to the entire. Instance; carbonate of potash will part with a portion of its carbonic acid in a moderate degree of heat, yet it requires a very strong heat to expel the whole. In like manner crystallized sulphate of potash will part with most of its water in a heat below ignition, but it requires a strong red heat to drive away the entire of its water. Thus we find in proportion as the potash is deprived of one part of its carbonic acid, its power of retaining the remainder is increased: and the same holds good as to the expulsion of water from the salt. I shall forbear mentioning several other circumstances of the like nature."

The Doctor should at least glance at the work in which those important ideas first originated, and not attribute the principles on which they are founded to an author who cannot have the smallest pretensions to them.

It is very well known that I have done much for the antiphlogistic theory, that I have fixed it upon a more solid foundation

than

<sup>\*</sup> It would be very difficult to hit upon the degree of heat to ascertain the products so accurately as the Doctor describes.

<sup>↑</sup> See Essay on my Atomic Theory and Electrical Phænomena, page 64, or Comp. View, pages 40-41.

than Lavoisier himself had done; yet, as it originated with him, it belongs to him of right, and to him alone.

No person can prove that Mr. Dalton has made any novel or original addition to my Theory, except extending fancifully and hypothetically my relative weights of the ultimate particles of elementary matter, without sufficient proof to support his conjectures; at the same time that it is within the reach of accurate experimental knowledge to confirm the principles which I As to the relative weights or relative quantities of broached. matter in elementary particles, I cautiously confined myself to few instances, and those few will be found correct. They were deduced from the relative weights of simple and compound gases ; and I have pointed out exceptions, even to this mode of procedure : Instance,—nitrous air is lighter than the gaseous oxide of azote, and yet the atoms of the former are heavier than those of the latter; and I have lately pointed out that the particles of azote are nearly twice the weight of those of oxygen, although an equal volume of the latter gas is specifically heavier than that of azotic ges. I attributed these differences to the distances to which their particles or atoms are removed from each other by their respective atmospheres of caloric.

The relative proportions of ultimate particles in atoms and molecules were illustrated by many examples in my Comp. View, which constitutes another essential part of my system. The next and the most important part of my doctrine relates to the relative forces with which ultimate particles and atoms unite to each other singly, and the modification of this law when they unite 1 and 2, or 1 and 3, or 1 and 4, &c. Were I to leave out this part, I could accomplish nothing decisive in my arduous investigation; and it enabled me to account for many phænomena and operations in chemistry which would otherwise be inexplicable.

The foregoing principles aggregately, but particularly the latter part, enabled me "to place chemistry on the same ground with that on which the discovery of the laws of gravity placed the science of astronomy."

This last link of my Theory Dalton overlooked altogether. I suppose he considered it too marked a feature to bring forward. But forward it must come, or else the Atomic Theory must remain a mere *bauble*.

In taking a cursory view, a few days ago, of the last edition (the fifth) of Dr. Thomson's System of Chemistry, I found that he transferred fny Atomic Theory to Dalton, without even mentioning my name; and, what is extraordinary, adduces as an example, my proportions of azote and oxygen in the different compounds of those elements\*. The Doctor also gives some ex-

\* Vol. iii. p. 19.

periments

periments which were first made by me, and which helped very materially to illustrate the atomic theory or definite proportions, without the smallest reference to the author. I will adduce one, viz. the firing of oxygen and sulphuretted hydrogen by means of the electric spark, and the ascertaining of the products, &c.

In giving an history of the progress of the antiphlogistic theory and of the memorable contest which was carried on between the two sects of philosophers, he does not even glance at my Comparative View, which according to himself, in one of his Journals, operated so conspicuously and decisively against the arguments of my illustrious friend Kirwan. In giving an account of electrical phænomena, he passes over my hypothesis on that subject, although he adduces less probable ones of many other writers; and in his Account of Meteoric Stones, although I analysed one which fell in this kingdom; and although I advanced a new doctrine agreeable to my hypothesis of electrical phænomena, respecting the cause of their ignition, &c. he never once mentions my views. I could enumerate many more facts; but a sufficient number have been adduced to show a rooted prejudice, and a degree of glaring injustice not to be equalled in the history of any science. But the Doctor having, unfortunately to himself, commenced with his prejudices, he must persist; although we find him contradicting himself on many other occasions. A compiler of a science is an historian in that department, and he should detail his facts faithfully and impartially; he should not attempt to shove aside one experimenter, and to bring forward another of less pretensions; he should not attempt to suppress the labours of one man in order to confer them on his favourites. When a compiler deviates from those principles, he injures his readers, the science, and ultimately himself.

The Doctor, it is true, was generous enough to allow me a few facts; facts so insulated or so detached from the important objects to which they belonged in my system, that they appear singly of little or no consequence. To make use of the expression of a learned acquaintance of mine, "The Doctor extinguished your great lights, and furnished you with the feeble glimmer of a rush-light."

I am, sir,

Your obedient humble servant,

Dublin, Feb. 4, 1818.

WILLIAM HIGGINS.

XXIX. Mr.