# Joseph Priestley (1733-1804)

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# CONSIDERATIONS

ON THE

## *DOCTRINE*

OF

# PHLOGISTON

AND

# *The Decomposition of Water*

**BY JOSEPH PRIESTLEY, *LL.D. F.R.S. &c. &c.***

*Qualem commendes etiam atque etiam aspice.* HORACE.

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**1796**

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To Messrs. Berthollet, De la Place, Monge, Morveau, Fourcroy, and Hassenfratz,
The surviving Answerers of Mr. Kirwan.

Gentlemen,

Having drawn up a short defense of the doctrine of *phlogiston*, I take the liberty of inscribing it to *you*, as the principal advocates for the Antiphlogistic theory. My view in this is to draw your attention once more to the subject, and I request the favour of an answer to my objections. I hope I am not wanting in a proper deference to the opinion of men so justly eminent as yourselves and your friends in France, and also that of great numbers in England, and wherever chemistry is known, who have adopted your hypothesis. But you will agree with me, that no man ought to surrender his own judgment to any mere *authority*, however respectable. Otherwise, our own system would never have been advanced.

As you would not, I am persuaded, have your reign to resemble that of *Robespierre*, few as we are who remain disaffected, we hope you had rather gain us by persuasion, than silence us by power. And though we are all apt to flatter ourselves, we hope we are as willing to be influenced by the former, as we are inflexible to the latter. If you gain as much by your answer to me, as you did by that to Mr. Kirwan, your power will be universally established, and there will be no *Vendée* in you dominions.

Differing as we do in this respect, we all agree in our wishes for the prevalence of *truth*, and also of *peace*, which is wanted as much for the interests of philosophy, as those of humanity. And on this account I earnestly wish success to the arms of France, which has done me the honour to adopt me when I was persecuted and rejected in my native country. With great satisfaction, therefore, I subscribe myself

Your fellow-citizen,
Joseph Priestley

Northumberland in America,
June 15th, 1796.

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# CONSIDERATIONS ON THE DOCTRINE OF PHLOGISTON, AND THE DECOMPOSITION OF WATER

There have been few, if any, revolutions in science so great, so sudden, and so general, as the prevalence of what is now usually termed *the new system of chemistry*, or that of the *Antiphlogistians*, over the doctrine of Stahl, which was at one time thought to have been the greatest discovery that had ever been made in the science. I remember hearing Mr. Peter Woulfe, whose knowledge of chemistry will not be questioned, say, that there had hardly been any thing that deserved to be called a *discovery* subsequent to it. Though there had been some who occasionally expressed doubts of the existence of such a principle as that of *phlogiston*, nothing had been advanced that could have laid the foundation of another system before the labours of Mr. Lavoisier and his friends, from whom this new system is often called that of the *French*.

This system had hardly been published in France, before the principal philosophers and chemists of England, notwithstanding the rivalship which has long subsisted between the two countries, eagerly adopted it. Dr. Black in Edinburgh, and as far as I hear all the Scots have declared themselves converts and what is more, the same has been done by Mr. Kirwan, who wrote a pretty large treatise in opposition to it. The English reviewers of books, I perceive, universally favour the new doctrine. In America also, I hear of nothing else. It is taught, I believe, in all the schools on this continent, and the old system is entirely exploded. And now that Dr. Crawford is dead, I hardly know of any person, except my friends of the Lunar Society at Birmingham, who adhere to the doctrine of phlogiston; and what may now be the case with *them*, in this age of revolutions, philosophical as well as civil, I will not at this distance answer for.

It is no doubt *time*, and of course opportunity of examination and discussion, that gives stability to any principles. But this new theory has not only kept its ground, but has been constantly and uniformly advancing in reputation, more than *ten years*, which, as the attention of so many persons, the best judges of everything relating to the subject has been unremittingly given to it, is no inconsiderable period. Every year of the last twenty or thirty has been of more importance to science, and especially to chemistry, than any ten in the preceding century. So firmly established has this new theory been considered, that a *new nomenclature*, entirely founded upon it, has been invented, and is now almost in universal use; so that, whether adopt the new system or not, we are under the necessity of learning the new language, if we would understand some of the most valuable of modern publications.

In this state of things, an advocate for the old system has but little prospect of obtaining a patient hearing. And yet, not having seen sufficient reason to change my opinion, and knowing that free discussion must always be favourable to the cause of truth, I wish to make one appeal more to the philosophical world on the subject, though I have nothing materially new to advance. For I cannot help thinking that what I have observed in several of my publications has not been duly attended to, or well understood. I shall therefore endeavour to bring into one view what appears to me of the greatest weight, avoiding all extraneous and unimportant matter; and perhaps it may be the means of bringing out something more decisive in point of *fact*, or of *argument*, than has hitherto appeared.

No person acquainted with my philosophical publications can say that I appear to have been particularly attached to any hypothesis, as I have frequently avowed a change of opinion, and have more than once expressed an inclination for the new theory, especially that very important part of it the *decomposition of water*, for which I was an advocate when I published the sixth volume of my experiments; though farther reflection on the subject has led me to revert to the creed of the school in which I was educated, if in this respect I can be said to have been educated in any school. However, whether this new theory shall appear to

be well founded or not, the advancing of it will always be considered as having been of great importance in chemistry, from the attention which it has excited, and the many new experiments which it has occasioned, owing to the just celebrity of its patrons and admirers.

SECTION I.

## *Of the Constitution of Metals*

According to the doctrine of phlogiston, advanced by Becher and Stahl in the beginning of this century, and much simplified and improved since their time, metals, phosphorus, sulphur, and many other substances which are supposed to contain it, are compounds, consisting of this principle, and another which may be called its *base*. Thus each of the metals contains phlogiston united to a peculiar calx, and sulphur and phosphorus consist of the same principle and their respective acid, or the bases of them. But according to the antiphlogistic theory, all the metals are simple substances, and become calces by imbibing pure air; and sulphur and phosphorus are also simple substances, and become the acid of vitriol and of phosphorus by imbibing the same principle, called by them *oxygen*, or the principle, as it probably is, or universal acidity.

As a proof that metals are simple substances, and that they become calces merely by imbibing air, they allege the case of mercury, which becomes the calx called *precipitate per se* by exposure to the atmosphere in a certain degree of heat, and which becomes running mercury again by exposure to a greater degree of heat. They therefore think it impossible not to conclude, that in all other cases of calcination, as well as this, the only difference between the calx and the metal, is that the latter has parted with the air which it has imbibed.

But this is the case of only this particular calx of this metal, and there is another calx of the same metal, viz. that which remains after exposing turbith mineral to a red heat, which cannot be completely revived by any degree of heat, but may be revived in inflammable air, which it imbibes, or when mixed with charcoal, iron-filings, or other substances supposed to contain phlogiston. And if this calx of mercury, or (supposing it to contain some acid of vitriol) this salt, necessarily requires some addition to constitute it a metal, all mercury must contain the same. For though with the same external appearance, the same metal may contain different proportions of any particular principle, as phlogiston, they must be denominated different substances, if some specimens contain this element, and others be wholly destitute of it. All, therefore, that can be inferred from the experiment with the precipitate per se is, that in this particular case, the mercury in becoming that calx imbibed air, without parting with any, or very little, of its phlogiston; and if we judge by the air expelled from the calces of metals and other circumstances, there are few, if any, of them but contain more or less of phlogiston.

I would observe in this place, that it is asserted by some very able chemists, that if the precipitate per se be made with proper attention, it will be revived without yielding any air. This is also the case with *minium* when fresh made. But this is owing, I doubt not, to their wanting *water*, which I deem to be essential to the constitution of every kind of air; so that they both contain the element of dephlogisticated air, though, for want of water, it is not able to assume that form.

That mercury may have the same external appearance, and all its essential properties, and yet contain different proportions of something that enters into it, is evident from the phenomena of its solution in the nitrous acid, and the revival of its calx in inflammable air. According to the old theory, there is a loss of some part of its phlogiston in the solution of mercury in the nitrous acid, since nitrous air is procured in the process. And though it may be revived from its precipitates by mere heat, yet if it be revived in a vessel of inflammable air, it will imbibe it in great quantities. Mercury revived in these circumstances must contain more phlogiston that that which is revived from the same calx by mere heat. But though mercury revived by mere heat after a solution in nitrous acid must have a deficiency of phlogiston, and when it is revived from precipitate per se in inflammable air must contain a redundancy of the same principle, yet there will hardly be a doubt but that, in all chemical processes, it would exhibit the same phenomena.

In all other cases of the calcination of metals in air, which I have called the *phlogistication* of the air, it is not only evident that they gain something, which adds to their weight, but that they likewise part with something. The most simple of these processes is the exposing iron to the heat of a burning lens in confined air, in consequence of which the air is diminished, and the iron becomes a calx. But that there is something emitted

from the iron in this process is evident from the strong *smell* which arises from it. If the process be continued, inflammable air will be produced, if there be any moisture at hand to form the basis of it. From this it is at least probable, that, as the process went on in an uniform manner, the same substance, viz. the basis of inflammable air, was continually issuing from it; and this is the substance, or principle, to which we give the name of *phlogiston*.

That the effect of this process is not, as the antiphlogistians assert, the mere separation of the dephlogisticated from the phlogisticated air in that of the atmosphere, I have proved in a course of experiments, in which I have shown that a considerable part of the phlogisticated air that is found after this process is formed in the course of it, by the union of the phlogiston from the iron with the dephlogisticated air. And if the calcination of the iron in this process be always attended with the loss of some constituent part of it, the same is, no doubt, the case with all other calcinations of the same metal, and also those of all other metals. And farther, if the *metals* be compound substances, containing phlogiston united to some base, the same is the case with *sulphur* and *phosphorus*, because they become acids when they are used in the same process.

According to the antiphlogistic theory, the inflammable air that is produced in the solution of metals in any acid comes wholly from the water combined with it, and not at all from the metal dissolved. But the advocates for this theory do not seem to have attended to one necessary consequence of this supposition. According to their own principles, water consists of eighty-seven parts of oxygen, to only thirteen of hydrogen, in every hundred, which is nearly seven times as much of the former as of the latter. Consequently, since nothing but hydrogen escapes in the process, there must remain, from this decomposition of the water, seven times as much oxygen in the solution. But both Mr. Lavoisier and Mr. de la Place say, what I doubt not is strictly true, that after the process the acid will saturate exactly the same quantity (they do not say more) of alkali, that it would have done before; whereas, with the addition of so much oxygen, it ought to saturate considerably more. If the oxygen from the decomposition of the water do not join that in the acid, what becomes of it?

If this case be analogous to that of the supposed decomposition of water by hot iron, the oxygen ought to be lodged in the iron, and compose finery cinder (magnetic oxide of iron). But this substance is not soluble in vitriolic acid, if that be employed in the experiment; and when it is dissolved in the marine acid, it does not dephlogisticate it, as minium, and other substances containing oxygen, do. It is evident, therefore, that there is no addition of oxygen in this process, consequently no decomposition of water in the case, and that the inflammable air must come from the decomposition of the iron.

SECTION II

## *Of the Composition and Decomposition of Water*

The antiphlogistic theory has received its greatest support from the supposed discovery that water is resolvable into two principles, one that of *oxygen*, the base of dephlogisticated air, and the other, because it has no other origin than water, *hydrogen*, or that which, with the addition of calorique, or the element of *heat*, constitutes inflammable air. "One of the parts of the modern doctrine the most solidly established, say Mr. Berthollet, and the other authors of the *Report* on this subject is the formation, the decomposition, and recomposition, of water. And how can we doubt of it, when we see that, in burning together fifteen grains of inflammable air, and eighty-five of vital air, we obtain exactly an hundred grains of water, in which, by decomposition, we find again the same principles, and in the same proportions. If we doubt of a truth established by experiments so simple, and palpable, there would be nothing certain in natural philosophy. We might even question whether vitriolated tartar be composed of vitriolic acid and fixed alkali, or sal ammoniac of the marine acid and volatile alkali, etc., etc. For the proofs that we have of the composition of these salts are of the same kind, and not more rigorous, than those which establish the composition of water. Nothing perhaps more clearly proves the weakness of the old theory, than the forced explanations that have been attempted to be given of these experiments."

Notwithstanding the confidence thus strongly expressed by these able and experienced chemists, I must take the liberty to say, that the experiments to which they allude appear to me to be very liable to exception, and that the doctrine of phlogiston easily accounts for all that they observed.

Their proof that water is decomposed, and resolved into two kinds of air, is that when steam is made to pass

over red-hot iron inflammable air is produced, and the iron acquires an addition of weight, becoming what is called *finery cinder*; but what they call oxide of iron, supposing that there is lodged in it the oxygen which was one of the constituent parts of the water expended in the process, while the other part, or the hydrogen, with the addition of heat, assumed the form of inflammable air.

But in order to prove that this addition of weight to the iron is really oxygen, they ought to be able to exhibit it in the form of dephlogisticated air, or of some other substance into which oxygen is allowed to enter, and this they have not done. Iron that has really imbibed air, or the common *rust of iron*, has a very different appearance from this finery cinder, being *red*, and not *black*; and when treated in similar processes, exhibits very different results. Mr. Fourcroy says that this finery cinder is "iron partially oxygenated." But if that were the case, it would go on to attract more oxygen, and in time become a proper rust of iron, completely oxygenated. But this is so far from being the case, that finery cinder never will acquire rust; which shows that the iron in this state is saturated with some very different principle, which even excludes that which would have converted it to rust.

However, neither this, nor any other calx of iron, can be revived unless it be heated in inflammable air, which it eagerly imbibes, or in contact with some other substance which has been supposed to contain phlogiston. The probability there is, that the phlogiston then enters this calx of iron, replacing that which had been expelled to form the inflammable air. Nor can any inflammable air be procured in this process with steam, but by means of some substance which has been supposed to contain phlogiston. Where then, is the certain proof that water is decomposed in this process?

It may be said that the oxygen imbibed by this iron, being expelled by heat in contact with inflammable air, unites with that air, and with it constitutes the water which is found after the process. But for any thing that appears, this water may be that which the iron had imbibed, and which can only be expelled from it by the entrance of that phlogiston which it had lost.

This is the more probable, since, when any other substance which is certainly known to contain oxygen, is heated in the same circumstances, *fixed air* (which is allowed to contain oxygen) is found, and this is not the case with this calx of iron. If, for example, precipitate per se, or minium, be heated in inflammable air, the mercury and the lead will be revived, and a considerable quantity of fixed air will be produced at the same time. But if the air be previously expelled from the minium, which converts it into a yellow substance called *massicot*, though the lead will be revived, no fixed air will be generated. Since, therefore, the result of treating finery cinder and massicot is precisely the same, in the same circumstances, we are fully authorized to conclude that the substances themselves are similar, and consequently that the finery cinder contains no more oxygen than massicot.

In another important respect finery cinder and massicot are similar. They are both soluble in marine acid without dephlogisticating it, which minium instantly does. And yet Mr. Berthollet says, *Annales de Chimie*, Vol. 3, p. 96, that "the heat by which minium becomes massicot cannot change its nature." What is the evidence of a change in the *nature* of any thing, but a change of its *properties*? On the whole, therefore, the probability is, that when iron is converted into finery cinder, it loses its phlogiston, and imbibes only water; and that when it is reconverted into iron, it parts with the water, and recovers its phlogiston. N.B. The experiment with the massicot must be tried presently after it is made, since it will very soon imbibe air from the atmosphere.

In this place I would observe that, if it be admitted that there is a principle in inflammable air, which, being imbibed by the calx of a metal, converts it into a metallic substance, it will follow that the same principle is contained in charcoal, and other combustible substances; because they will all produce the same effect, and therefore that the principle of inflammability, or phlogiston, is the same in them all.

Another pretended proof that water is composed of dephlogisticated and inflammable air, is that when the latter is burned slowly in the former, they both disappear, and a quantity of water is produced, equal to their weight. I do not, however, find that it was in more than a single experiment that water so produced is said to have been entirely free from acidity, though this experiment was on a large scale, not less than twelve ounces of water being procured. But the apparatus employed does not appear to me to admit of so much accuracy as the conclusion requires; and there is too much of correction, allowance, and computation, in deducing the

result. Also it is, after all, acknowledged that, after decomposing this quantity of the two kinds of air, and making all the allowance they could for the phlogisticated air, or azote, in the dephlogisticated air, they found fifty-one cubic inches of this kind of air more than they could well account for. This quantity, therefore, and perhaps something more (since the operators were interested to make it as small as possible) must have been formed in the process. And when this kind of air, as well as inflammable, is decomposed together with dephlogisticated air, nitrous acid is produced. The probability therefore is, that the acidifying principle, or oxygen, in the dephlogisticated air which they decomposed, was contained in that phlogisticated air, and that, had the process been conducted in any other manner, it would have assumed the form of nitrous acid. They acknowledge that, except when the inflammable air was burned *in the slowest manner*, the water they produced had more or less of acidity.

The experiments which I made on the decomposition of these two kinds of air in *close vessels*, appear to me to be much less liable to exception, and the conclusion drawn from them is the reverse of that of the French philosophers.

When dephlogisticated and inflammable air, in the proportion of a little more than one measure of the former to two of the latter, both so pure as to contain no sensible quantity of phlogisticated air, are inclosed in a glass or copper vessel, and decomposed by taking an electric spark in it, a highly phlogisticated nitrous acid is instantly produced; and the purer the airs are, the stronger is the acid found to be. If phlogisticated air be purposely introduced into this mixture of dephlogisticated and inflammable air, it is not affected by the process, though, when there is a considerable deficiency of inflammable air, the dephlogisticated air, for want of it, will unite with the phlogisticated air, and, as in Mr. Cavendish's experiment, form the same acid. But since both kinds of air, viz. the inflammable and the phlogisticated, contribute to form the same acid, they must contain the same principle, viz. phlogiston.

If there be a redundancy of inflammable air in this process, no acid will be produced, as in the great experiment of the French chemists, but in the place of it there will be a quantity of phlogisticated air. A considerable quantity of *water* is always produced in these decompositions of air. But this circumstance only proves that the greatest part of the *weight* of all kinds of air is water. I have, in my experiments on *terra ponderosa aerata* demonstrated that water constitutes about half the weight of fixed air.

When the decomposition of dephlogisticated and inflammable air is made in a glass vessel, a peculiarly *dense vapour* is formed, which the eye can easily distinguish not to be mere vapour of *water*, and if the juice of turnsole be put into the vessel, it immediately becomes of a deep red, which shows that it was an acid vapour.

Since the acid that I procured in this process was in considerable quantity, and no phlogisticated air was present (for in the last of my experiments I did not even make use of an air-pump, but first filled the vessel with water, and then displaced it by the mixture of the airs), I do not see how it is possible to account for the formation of this acid but from the union of the two kinds of air; and it can hardly be supposed that, in the very same process, the decomposition of the same substances should compose others so very different from each other as *water* and *spirit of nitre*. I think I have sufficiently accounted for the result of the experiments made by the French chemists on the common hypothesis, which supposes inflammable air to contain phlogiston; but I do not yet see how it is possible for them to explain mine on theirs, according to which there is no such principle in nature. Upon the whole, it does not appear to me that the evidence either for the composition, or the decomposition, of water, is at all satisfactory; and certainly the arguments in support of an hypothesis so extraordinary, and so novel, ought to be of the most conclusive kind.

SECTION III

## *Other Objections to the Antiphlogistic Theory*

Having considered the evidence that has been alleged in support of the antiphlogistic theory, and found it to be insufficient, I shall, in this section, mention a few objections that may be made to it from other considerations.

1. If inflammable air, or hydrogen, be nothing more than a component part of water, it could never be produced but in circumstances in which either water itself, or something into which water is known to enter, is

present. But in my experiments on heating finery cinder together with charcoal, inflammable air is produced, though, according to the new theory, no water is concerned. According to this theory, finery cinder, called the *oxide of iron*, consists of nothing besides iron and oxygen; and the charcoal, made with the greatest degree of heat that can be applied, is equally free from water; and yet when these two substances are mixed together, and exposed to heat, they yield inflammable air in the greatest abundance.

This fact I cannot account for on the principles of the new theory; but nothing is easier on those of the old. For the finery cinder containing water, as one of its component parts, gives it out to any substance from which it can receive phlogiston in return. The water, therefore, from the finery cinder uniting with the charcoal makes the inflammable air, at the same time that part of the phlogiston from the charcoal contributes to revive the iron. Inflammable air of the very same kind is produced when steam is made to pass over red-hot charcoal.

2. Though the new theory discards phlogiston, and in this respect is more simple than the old, it admits another new principle, to which its advocates give the name of *carbone*, which they define to be the same thing with charcoal, free from earth, salts, and all other extraneous substances; and whereas we say that fixed air consists of inflammable air and dephlogisticated air or oxygen, they say that it consists of this carbone dissolved in dephlogisticated air. Mr. Lavoisier says that "wherever fixed air has been obtained, there is charcoal." They therefore call it the *carbonic acid*.

But in many of my experiments large quantities of fixed air have been procured where neither charcoal, nor any thing containing charcoal, was concerned, or none in quantity sufficient to account for it. When the purest malleable iron is heated in dephlogisticated air, or in vitriolic acid air, a considerable quantity of fixed air is formed. It is said that plumbago is contained in iron. But it is not found in malleable iron, and least of all in the air that is expelled from it. Fixed air is also produced by reviving minium in inflammable air, and if charcoal of copper be heated in dephlogisticated air, a quantity of fixed air equal to nine-tenths of the dephlogisticated air will be formed. More than thirty ounce measures of the purest fixed air were by this means procured from six grains of this charcoal, which is made by the union of spirit of wine and this metal.

Lastly, fixed air is procured in great abundance in animal respiration. It is true that fixed air is procured by exposing lime-water to atmospherical air, but it is never procured by this means in air confined in any vessel. There must, for this purpose, be an open communication with the atmosphere. but fixed air will be procured in great abundance by breathing air contained in the smallest receiver, and especially if the air be dephlogisticated. It must therefore be formed by phlogiston, or something emitted from the lungs, uniting with the dephlogistcated air which it meets there. It may be said that since we feed in a great measure upon vegetables (and even animal food is originally formed from them) and this principle of *carbone* is found in all vegetables, *this* may be the substance that is exhaled from the lungs. But since, in this process, it forms the same substance that inflammable air from iron does with dephlogisticated air, or oxygen, it must be the same thing with it; and then this *carbone* will only be another name for *phlogiston*.

3. The antiphlogistians always suppose azote, or phlogisticated air, to be a simple substance, though I think abundant evidence has been given (and more will be found in my last memoir, printed in the *Transactions of the Philosophical Society at Philadelphia*), that it is composed of phlogiston and dephlogisticated air.

4. As to the *new nomenclature*, adapted to the new theory, no objection would be made to it, if it were formed, as is pretended, upon a knowledge of the real constitution of natural substances; but we cannot adopt one, the principles of which we conceive not to be sufficiently ascertained. For other objections to this nomenclature, I refer to the Preface to *Mr. Keir's* excellent *Dictionary of Chemistry*. However, whether we approve of this new language or not, it is now so generally adopted, that we are under a necessity of learning, though not of using it.

On the whole, I cannot help saying, that it appears to me not a little extraordinary, that a theory so new, and of such importance, overturning every thing that was thought to be the best established chemistry, should rest on so very narrow and precarious a foundation, the experiments adduced in support of it being not only ambiguous, or explicable on either hypothesis, but exceedingly few. I think I have recited them all, and that on which the greatest stress is laid, viz. that of the formation of water from the decomposition of the two kinds of air, has not been sufficiently repeated. Indeed, it requires so difficult and expensive an apparatus, and so

many precautions in the use of it, that the frequent repetition of the experiment cannot be expected; and in these circumstances the practiced experimenter cannot help suspecting the accuracy of the result, and consequently the certainty of the conclusion.

But I check myself. It does not become one on a minority, and especially of so small a minority, to speak or write with confidence; and though I have endeavoured to keep my eyes open, and to be as attentive as I could to every thing that has been done in this business, I may have overlooked some circumstances which have impressed the minds of others, and their sagacity is at least equal to mine.

The phlogistic theory is not without its difficulties. The chief of them is that we are not able to ascertain the *weight* of phlogiston, or indeed that of the oxygenous principle. But neither do any of us pretend to have weighed *light*, or the element of *heat*, though we do not doubt but that they are properly *substances*, capable by their addition, or abstraction, of making great changes in the properties of bodies, and of being transmitted from one substance to another.

N.B. For answers to the objections of Mr. Lavoisier and Mr. Berthollet to some experiments of mine relating to this subject, I refer to the last edition of my *Observations on Air*. Vol. III. p. 554.

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