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XXI. *On the Decomposition of Carbonic Acid Gas and the Alkaline Carbonates, by the Light of the Sun; and on the Tithonotype.* By JOHN W. DRAPER, M.D., Professor of Chemistry in the University of New York\*.

FOR many years it has been known that the green parts of plants under the influence of the sunlight possess the power of decomposing carbonic acid and setting free its oxygen. It is remarkable that this, which is a fundamental fact in vegetable physiology, should not have been investigated in an accurate manner. The statements met with in the books are often far from being correct. It is sometimes said that pure oxygen gas is evolved, that the decomposition is brought about by the so called "chemical rays;" these, and a multitude of other such errors pass current. So far as my reading goes no one has yet attempted an analysis of the phænomenon by the aid of the prism, the only way in which it can be truly discussed.

In a paper by Dr. Daubeny, inserted in the Philosophical Transactions for 1836 †, two facts which I shall verify in this communication are fully established. These are,—1st, the constant occurrence of nitrogen gas in mixture with the oxygen, an observation originally due to Saussure, or some earlier writer; and, 2nd, that the act of decomposition is due to the LIGHT of the sun. This latter result, obtained by employing coloured glasses or absorbent media, has not been generally received. Doubt will always hang about results obtained in this way, and nothing but an analysis by the prism can be satisfactory. It has happened, therefore, in books of credit published since that time, that other interpretations of the phænomena have been given. (Johnston's Agr. Chem., Lect. 5. § 7.) (Graham's Chem., p. 1013.)

\* Communicated by the Author.

† Noticed in Phil. Mag. S. 3. vol. viii. p. 416.—EDIT.

Phil. Mag. S. 3. Vol. 23. No. 151. Sept. 1843. M

In its connexions with modern organic chemistry and physiology the experiment of the decomposition of carbonic acid by leaves assumes extraordinary interest. To no other single experiment can the same importance be attached. When we remember that this decomposition is the starting-point for organization out of dead matter, that commencing with this action of the leaf the series of organized atoms goes forward in increasing complexity, and blood, and flesh, and cerebral matter are at its terminus, it is clear that unusual importance belongs to precise views of this the commencing change. The beams of the sun are the authors of all organization.

There is but one way by which the question can be finally settled, and that is by conducting the experiment in the prismatic spectrum itself. When we consider the feebleness of effect which takes place, by reason of the dispersion of the incident beam through the action of the prism, and the great loss of light through reflexion from its surface, it might appear a difficult operation to effect a determination in this way. Encouraged, however, by the purity of the skies in America, I made the trial and have met with complete success.

Before entering on the experiments which I have to communicate, I cannot avoid once more impressively calling the attention of chemists to the true character of those emanations which are here designated "tithonic rays." It is not enough that we admit the existence, throughout the spectrum, of dark rays, possessing the power of bringing about chemical changes; it is not enough that we call them chemical rays; there are qualities of distinction appertaining to them which mark them out as being specific in their kind, properties which they possess totally distinct from those of light and heat. Their title to the rank of a distinct imponderable agent is just as perfect as that of light or heat. From heat they are to be distinguished by incapacity for metallic conduction, and by want of the power of expanding bodies; from light by failing to give any impression to the organ of vision. According to the recognized rules of chemistry they ought to be received as a fourth imponderable agent.

It is not sufficient, as has been said, to call them "chemical rays." The term implies that the distinctive characteristic pertaining to them is the power of changing the composition of bodies. But do not the rays of heat eminently produce like changes? Are not half the decompositions in chemistry brought about by the action of caloric? As respects LIGHT, many instances are already known in which it produces decompositions and combinations; as will be presently shown,

it is the agent that brings about the decomposition of carbonic acid. The faculty of producing like effect is not the distinguishing quality of the tithonic rays, nor can the term *chemical* be any more applied to them than to either of their acknowledged distinct companions. *Unless therefore chemists are content to admit that a species of heat may exist devoid of the power of expanding bodies, of giving the sensation of warmth, and of being transmitted by conducting processes; or, unless they admit that light can exist in such a modified condition as to produce in our eyes the sensation of darkness, they will have to admit these tithonic rays as constituting a fourth imponderable agent.* The name they may take is not a matter of importance, that which is least trammelled by hypothesis is best. It is not the object of the papers I have written in this Journal to show merely that a class of invisible rays exists in the spectrum; that has been known for a long time; but it is to point out the true relation of these rays to other bodies and other forces in the world, to assert for them their title of a fourth distinct imponderable agent, and to secure for them the admission of that title by giving them a name.

When the leaves of plants are placed in water from which all air has been expelled by boiling, and exposed to the sun's rays, no gas whatever is evolved from them. When they are placed in common spring or pump water bubbles quickly form, which when collected and analysed prove to be a mixture of oxygen and nitrogen gases; from a given quantity of water a fixed quantity of air is produced. When they are exposed in water which has been boiled and then impregnated with carbonic acid, the decomposition goes on with rapidity, and large quantities of gas are evolved.

The obvious inference which seems to arise from these facts is, that all the oxygen collected is derived from the direct decomposition of carbonic acid. We shall presently examine whether this is the correct inference.

Having, by long boiling and subsequent cooling, obtained water free from dissolved air, I saturated it with carbonic acid gas. Some grass leaves, the surfaces of which were carefully freed from any adhering bubbles or films of air by having been kept beneath carbonated water for three or four days, were provided. Seven glass tubes, each half an inch in diameter and six inches long, were filled with carbonated water, and into the upper part of each the same number of blades of grass were placed, care being taken to have all as near as could be alike. The tubes were inserted side by side in a small pneumatic trough of porcelain. It is to be particularly remarked that the blades were of a pure green aspect as seen

in the water; no glistening air-film, such as is always on freshly-gathered leaves, nor any air bubbles were attached to them. Great care was taken to secure this perfect freedom from air at the outset of the experiments.

The little trough was now placed in such a position that a solar spectrum, kept motionless by a heliostat and dispersed by a flint glass prism in a horizontal direction, fell upon the tubes. By bringing the trough nearer to the prism or moving it further off, the different coloured spaces could be made to fall at pleasure on the inverted tubes. The beam of light was about three-fourths of an inch in diameter. In a few minutes after the commencement of the experiment, the tubes on which the orange, yellow, and green light fell, commenced giving off minute gas bubbles, and in about an hour and a half a quantity was collected sufficient for accurate measurement.

The gas, thus collected in each tube, having been transferred to another vessel and its quantity determined, the little trough with all its tubes was freely exposed to the sunshine. All the tubes now commenced actively evolving gas, which when collected and measured served to show the capacity of each tube for carrying on the process. If the leaves in one were more sluggish or exposed a smaller surface than the others, the quantity of gas evolved in that tube was correspondingly less. As may be readily supposed, I never could get tubes so arranged as to act *precisely* alike, but after a little practice I brought them sufficiently near to equality. And in no instance was this testing process of the power of each tube for evolving gas omitted after the experiment in the spectrum was over.

*Table of the Decomposition of Carbonic Acid by Light of different Colours.*

Experiment 1.		Experiment 2.	
Name of Ray.	Volume of Gas.	Name of Ray.	Volume of Gas.
Extreme red .....	·33	Extreme R. and red	·00
Red and orange...	20·00	Red and orange ...	24·75
Yellow and green	36·00	Yellow and green...	43·75
Green and blue...	·10	Green and blue ...	4·10
Blue .....	·00	Blue .....	1·00
Indigo .....	·00	Indigo .....	·00
Violet.....	·00	Violet ... ..	·00

From this it appears, that the rays which cause the decomposition of carbonic acid gas have the same place in the spectrum as the orange, the yellow, and the green,—the extreme

red, the blue, the indigo, and the violet, exerting no perceptible effect. This being the case, we should expect that by passing a beam through absorbent media of such a nature that the extreme red, the blue, the indigo, and violet are absorbed, this decomposition should nevertheless go on. A solution of bichromate of potash nearly fulfils these conditions, and not only does it absorb the luminous rays in question, but also all the tithonic rays, except a trace of those which correspond to the more refrangible yellow and less refrangible green.

A remarkable proof of the correctness of the foregoing prismatic analysis comes out when leaves are made to act on carbonated water in light which has passed through a solution of bichromate of potash. I took a wooden box of about a cubic foot in dimensions, and having removed its bottom, adjusted to it a trough made of pieces of plate glass. The box being set on end, its lid served as a door, and the trough being filled with a solution of bichromate of potash, the sun's beams came through it, and in the interior of the box an arrangement of leaves and carbonated water could be exposed to the rays that had escaped absorption. The thickness of the liquid stratum was about half an inch. I had several such boxes made, so that I might compare the simultaneous effect of light which had undergone absorption by different media. They formed, as it were, a series of little closets in which bodies could be exposed to party-coloured light—blue, yellow, red, &c.

Whenever an experiment was commenced in these closets, simultaneously a similar one was commenced in the unobstructed sunshine. It is needless to repeat, that in all these care was taken to have the different arrangements for decomposition as nearly alike as possible.

On comparing together the amount of gas evolved in unabsorbed light and in light that had undergone absorption by the bichromate of potash, in three out of five trials the gas collected under the latter circumstances exceeded in volume that collected under the former; this was probably due to a slightly higher temperature which obtained in the box.

On comparing together the volumes of gas collected under the bichromate of potash and under litmus water, the latter was not equal to one-half the former.

I compared together the gas evolved in unobstructed light, under bichromate of potash, and under ammonio-sulphate of copper; the results were as follows:—

Unobstructed light .....	4·75
Bichromate of potash .....	4·25
Ammonio-sulphate of copper	·75

Comparing these experiments, made by the aid of absorptive media, with those made by the prism, we are enabled to come to a definite conclusion as to the character of the rays which cause this decomposition.

The true office of prismatic analysis is to determine the refrangibility of the rays which produce given actions; but inasmuch as rays of heat, rays of light, and tithonic rays are found throughout the spectrum, in many cases the prism fails to indicate to which of these imponderable agents phænomena are to be ascribed. The case before us furnishes a striking example. Although the decomposition of carbonic acid is most energetically brought about by rays whose index of refraction corresponds to the yellow, yet that region of the spectrum is far from being devoid of heat and tithonicity.

By considering however the prismatic analysis and the absorptive analysis together, the following facts appear:—1st, the place of maximum action in the spectrum corresponds to the maximum of illumination; 2nd, at the place of the maximum of heat (which in the prism here used is beyond the extreme red) no decomposition whatever takes effect; this appears therefore to exclude calorific influence; 3rd, the point of maximum action of the tithonic rays, which escape absorption by the bichromate of potash, being towards the green, does not correspond with the place of maximum decomposition, which is the yellow; this seems to exclude the tithonic rays; 4th, the decomposition taking place almost as energetically under the bichromate of potash as in the unobstructed beams of the sun, and that salt absorbing all but a mere trace of the tithonic rays, if the effect was due to them it ought to be retarded to an extent corresponding to their loss by absorption, which is far from being the case; the retardation which is observed appearing to be attributable rather to the loss of light by reflexion from the faces of the trough, and the partial turbidity (want of translucence) of its glasses and solutions.

For these reasons I conclude that the decomposition of carbonic acid by the leaves of plants is brought about by the rays of LIGHT; and that the calorific and tithonic rays do not participate in the phænomenon. As was stated before, therefore, the rays of light are just as much entitled to the appellation of chemical rays as those which have heretofore passed under that name.

I might observe in passing, that there is a degree of precision attached to results of the decomposition of carbonic acid which is wholly wanting in most similar experiments. In the stains on Daguerreotype plates, or on photographic papers, though there is no difficulty in ascertaining the place of

maximum effect, yet nothing in the shape of absolute measures of quantities can be obtained. When however gas can be collected and its volume determined, as in the voltameter and in the experiments just described, the results possess a degree of exactness which enables us to draw from them definite conclusions.

Let us now proceed to determine the constitution of the gaseous mixture given off during their decompositions. It is not pure oxygen, as has often been supposed and often disproved, but a mixture of oxygen, nitrogen and carbonic acid. It is mainly to the ratio of the two former that attention has to be directed, the amount of the latter is always variable in different trials. Before proceeding to this there are certain observations to be premised, the results of which, though familiar to chemists accustomed to gaseous analysis, deserve a place here, for they seem to be wholly overlooked in many of the experiments connected with the so-called respiration, but rather digestion, of plants recorded in the books of botany.

When gas of any kind is confined over water in the pneumatic trough, its constitution is undergoing incessant change. A portion of it dissolves more or less slowly in the water, and in exchange it receives from the water gas which is always dissolved therein. If two jars, filled with different gases, stand side by side on the shelf, each is incessantly disturbing the constitution of the other, nor does this disturbance cease until the contents of both jars are chemically the same. There are some beautiful experiments of easy repetition which serve to show how rapidly gases and vapours can thus percolate through fluids. Take a pint bottle and pass through its cork, which ought to fit it very loosely, a glass tube a foot long, drawn narrow at its upper end. Into the bottle put a few drops of water of ammonia. Dip the wide end of the tube into a solution of soap, and introduce it into the interior of the bottle, adjusting it in such a position by the cork, that when air is blown in at the narrow end, the soap bubble which expands at the wide end may occupy the middle of the bottle. Placing the lips on the narrow end, blow a bubble an inch or more in diameter, and, without loss of time, cautiously draw back again the air from the interior of the bubble into the mouth. A strong ammoniacal taste is at once perceived. Now it is obvious that this ammonia must have passed with very great rapidity through the bubble.

A still more instructive experiment may be easily made. Take a three-ounce bottle with a wide neck, close the mouth of it by a film of soap water, by passing the moistened finger over it. Place it under a jar of protoxide of nitrogen. In-



stantly the horizontality of the film is disturbed; it swells upwards, and is spontaneously expanded by the passage of the gas through it into a bubble. The play of colour which attends this experiment, and the excessive thinness which the film finally assumes, render this one of the most beautiful experiments that chemistry can furnish; for when the bubble is almost invisible by reason of its incapacity to reflect light, and can only be seen in particular positions, it still discharges its percolating function.

This percolation of gases through liquids cannot be hindered by employing oil or such other liquids as botanical writers seem to imagine. Through common lamp oil, through copaiva balsam, &c., hydrogen gas will escape with rapidity, and protoxide of nitrogen and carbonic acid still faster. The law that regulates these phenomena is a very simple one,—the gas escapes through the confining medium with a rapidity proportional to its solubility therein.

These things being understood, it is obvious that when carbonic acid is decomposed in the experiments we have been detailing, a variable proportion of that gas will intermingle with the oxygen collected. The proportions must be variable, for it depends on the amount of carbonic acid remaining behind in the water, on the speed with which the experiment is conducted, and other variable conditions. As before stated, therefore, I shall leave out of consideration this carbonic acid, in discussing the analysis of the collected gases, because it is present by accident and is not essentially connected with the phenomena, except in one instance, where dark heat is to be employed, as will be described presently.

*Analysis of Air evolved from Carbonated Water by the Sun.*

Exp.	Name of Plant.	Oxygen.	Nitrogen.
1.	<i>Pinus tæda</i> .....	16·16	8·34
2.	do. ....	27·16	13·84
3.	do. ....	22·33	21·67
4.	<i>Poa annua</i> .....	90·00	10·00
5.	do. ....	77·90	22·10

I may remark that this table contains a few out of a great number of experiments, all of which might have been quoted as examples of the observations which I wish to deduce from it. 1st. They all coincide in this respect, that the oxygen is never evolved without the simultaneous appearance of nitrogen. 2nd. That when certain leaves are employed, as those of the *Pinus tæda*, there seems to be a very simple relation between the volumes of oxygen and nitrogen. In the first

and second of those experiments the volume of the oxygen is to that of the nitrogen as two to one; in the third as one to one. In certain cases this apparent simplicity of proportion is departed from; but from its frequent occurrence in many analyses I have made, it seems to demand attentive consideration. Moreover, in other plants, as in experiments 4 and 5, the amount of oxygen is relatively greater, and between it and the nitrogen there does not appear any exact proportion.

In order to ascertain whether decompositions taking place under absorbent media, as bichromate of potash, produce the same results as indicated in the foregoing table, I made several analyses of gas collected under these circumstances. The presence of the absorbent medium did not seem to exert any influence whatever, the general results coming out as though it had not been employed.

It has long been a matter of popular observation that the sunlight has the quality of extinguishing domestic fires. I do not know whether there is in reality any ground for this opinion; or if so, whether the phænomenon is in any way connected with the relations of light to carbon and oxygen. Popular opinion ascribes the effect to the light and not the heat of the ray. To determine whether radiant heat, unaccompanied by light, had the power of producing decomposition of carbonic acid through the agency of leaves, I placed in the focus of a large brass concave mirror a vessel containing some pine leaves in carbonated water. The mirror was set before a wood fire, and after a little time the leaves began evolving bubbles. The temperature of the water rose as high as  $140^{\circ}$  Fahr., and when sufficient gas was collected, examination proved that nearly the whole of it was absorbed by lime or potash water. From this it is evident that radiant heat merely liberates the carbonic acid, and does not decompose it. This corroborates therefore the result of pneumatic analysis, that it is the light and not the heat which brings about the change.

*Decomposition of Alkaline Salts.* — The conditions under which carbonic acid gas is decomposed being understood, I pass now to the description of similar decompositions occurring in the case of saline bodies. It has always been a subject of surprise to chemists, that the powerful affinity by which carbon and oxygen are held together should be so easily overcome at common temperatures. Even potassium cannot decompose carbonic acid in the cold. It might therefore be reasonably expected that the energetic forces which bring about this change ought also to effect other remarkable decompositions.

In fact, as I shall now proceed to show, the decomposition of carbonic acid is only one of a very numerous series.

The alkaline bicarbonates, as is well known, undergo decomposition by a slight elevation of temperature. When boiled with water they gradually give off their second atom of acid, and slowly pass into the condition of neutral carbonate. This easy decomposibility led me to inquire whether green leaves, under the action of the sunlight, would effect the liberation and subsequent reduction of the acid. In the following experiments it is to be observed, that the boiling is not continued long enough to affect to any extent the constitution of the salt, and in each case any portion of free carbonic acid extricated during the cooling of the liquid was removed by the action of the air-pump. The solution when finally used contained no gaseous matter, but only the salt dissolved in water.

Having boiled some distilled water to expel all gaseous matter, dissolve in it a small quantity of bicarbonate of soda. Introduce into a test tube some leaves of grass, fill the tube with the saline solution which has been once more boiled to expel any air it may have obtained from the dissolving salt, and invert the tube in some of the solution in a wine glass, after having carefully removed all adhering bubbles of air from the leaves by a piece of wire, or in any other convenient manner. This arrangement kept in the dark undergoes no change; but, if brought into the sunshine, bubbles of gas are rapidly evolved, and in the course of a few hours the tube becomes half-full. On detonation with hydrogen this gas proves to be rich in oxygen.

I made some attempts to discover how much oxygen could in this way be evolved from known quantities of bicarbonate of soda, supposing it probable that the second atom of carbonic acid being removed and decomposed, the process would cease. I need not detail the result of those trials; they indicated that the supposition I had formed was not correct. The process is not limited to the removal and decomposition of the second atom, but goes forward, the first atom itself being in like manner decomposed. From this it would seem that carbonate of soda itself should be decomposed, and experiment verifies the conclusion; for on using that salt instead of the bicarbonate, the evolution of oxygen goes on precisely in the same way.

As in these experiments *solid* salt dissolved in water is decomposed, it is obvious that the function by which the leaves accomplish this is very different from that of respiration. It is not respiration, but a true digestion.

Liebig has shown that ammonia exists in the ascending sap. It is probable, therefore, that it does not undergo final change before reaching the upper face (sky-face) of the leaf. There, if it be in the form of a carbonate, it unquestionably is concerned in decomposition. With the natural experiment before us, we might expect that the carbonate of ammonia used in place of the soda salts of the last experiment would yield like them. Accordingly it will be found, by using the officinal sesqui-carbonate of ammonia, that leaves effect its decomposition. In numerous experiments it has yielded me gas frequently containing more than 90 per cent. of oxygen.

In every instance which I have examined the gas evolved from leaves is not pure oxygen, but, as has been said, a variable mixture of oxygen and nitrogen. This result is of uniform occurrence; I have observed it in low latitudes where the sun is extremely brilliant, in the case of different plants; and on referring to Dr. Daubeny's paper, it will appear that he has uniformly recognized the same result in England. The very remarkable qualities which certain nitrogenized substances are known to exhibit, acting as ferments as they are undergoing decay, might lead to the suspicion that the decomposition of carbonic acid by leaves is due to the action of some nitrogenized body, the *eremacausis* of which is promoted by the rays of the sun.

There are many facts which go to prove that the decomposition of carbonic acid is a secondary result brought about by the action of a nitrogenized ferment in a state of *eremacausis*, the sunlight operating in the first instance upon the ferment itself. Plants can grow in a certain manner in dark places, and if the observations of botanists have been correctly made, although this kind of growth may be abnormal, it eventuates in increasing the total weight of carbon. It signifies little that in these instances lignin may often be deficient, for other bodies of the starch family make their appearance; and results of this kind serve to show that, though in all ordinary cases the union of carbon with the elements of water is an effect of light, there are other cases in which, either by ferment action, or other powers residing in the plant, the same result can be attained.

Boussingault states that grass leaves dried in air at 212° Fahr., and burnt with oxide of copper, yield 1.3 per cent. of their dry weight of nitrogen, which nitrogen is of course in combination. I found, however, that there is besides this, included in the tissue of the leaf, a certain quantity of gas which may be removed by the air-pump. I presume this air is naturally inclosed in the spiral vessels. When leaves are placed in an inverted jar with boiled water *in vacuo*, this gas is li-

berated; at first most copiously from the fractured extremity, but as the process of exhaustion goes on it exudes from both faces of the leaf, perhaps by rending open the frail tissue in which it is imprisoned. In leaves that have stomata on one side only, it does not pour forth from those organs in preference to other parts: and from this it may be inferred that it does not normally exist in the intercellular spaces. In a given weight of leaves its amount is very variable, ranging in my experiments from  $\cdot 01$  to  $\cdot 02$  cubic inch for ten grains of grass leaves. Its constitution as determined by analysis is also variable, but very remarkable; it contains from 88 to 94 per cent. of nitrogen.

It being therefore understood that in the tissue of the leaf a certain quantity of gas is mechanically included, which gas differs from atmospheric air in the circumstance that it contains a larger volume of nitrogen, which may be removed by the air-pump, we are in a condition to understand whether it is this nitrogen which furnishes the supply found in the gas exhaled by leaves. The following experiment proves that it is not.

I removed by continued boiling and exhaustion all the air dissolved in a solution of bicarbonate of soda. I also removed all the nitrogen from some grass leaves, by placing them *in vacuo* immersed in water that had been boiled and subsequently cooled. Then, placing these leaves in the solution of the bicarbonate and in the vessels in which the experiment was finally to be conducted, I kept them *in vacuo* for an hour. This was done to get rid of that film of atmospheric air which always adheres to the surface of glass vessels, and which might have disturbed the result by furnishing nitrogen. The leaves were now exposed in the saline solution to the beams of the sun, and presently the evolution of gas commenced. When a sufficient quantity was collected, it was found to consist of 88 per cent. oxygen and 12 nitrogen.

Repetitions of this experiment prove that although the nitrogen mechanically inclosed in the leaf to a certain extent mingles with the oxygen evolved, and indeed it could not be otherwise on account of the diffusion of gases into one another, yet the true source is to be sought in some nitrogenized compound present in the leaf, which is undergoing decomposition in a regulated way.

Keeping this fact clearly before us, that the source of the nitrogen found thus in company with the oxygen given off under the influence of light is some nitrogenized body existing in the leaf, the following experiments will show the simple and beautiful law under which this phænomenon is conducted.

Saussure has already determined, that when plants are forced to grow in an atmosphere of known volume, containing carbonic acid gas, after the decomposition of the gas is completed, the total volume remains unchanged. As my experiments were made with leaves immersed in water, I was desirous of proving whether under these forced circumstances the same result would still hold good.

To a certain quantity of water, from which all air had been expelled, confined in a jar over mercury, I passed 20 measures of carbonic acid gas; by a little agitation the water took up 15.50 measures of the acid. I now introduced into the jar some leaves, taking the greatest care that no bubbles of air should pass along with them. The jar was then placed in the sunshine, and the decomposition completed. Corrected for variation of temperature and pressure, the resulting volume of the gas in two experiments was 20, or precisely the same as that of the carbonic acid.

We may therefore infer that the volume of mixed gases evolved is precisely equal to the volume of carbonic acid that disappears. This leads us to some very remarkable conclusions.

When the leaves of plants under the influence of light decompose carbonic acid, they assimilate all the carbon, and a certain proportion of oxygen disappears, at the same time they emit a volume of nitrogen *equal to that of the oxygen consumed*.

This disappearance of oxygen and appearance of nitrogen are thus connected with each other; they are equivalent phenomena.

The emission of nitrogen is thus shown not to be a mere accidental result, but to be profoundly connected with the whole physiological action.

I arrive also at this conclusion from experiments of another kind. If the nitrogen that appears in company with oxygen were obtained by diffusion from gas mechanically shut up in the parenchyma of the leaf, it is plain, in the mode of operation which I have followed, in which leaves are immersed under water, and no opportunity given them of restoring their mechanically included air, if it were by any means withdrawn, that the first portions of mixed gas evolved should be richest in nitrogen, and that the per-centage amount should gradually become less and less, as it was removed from the structure of the leaf; this follows from the laws of the diffusion of gases. But this is far from being the case. It very commonly happens that more nitrogen is evolved *at the close of the process* than at its beginning. Thus, in one of the experiments I made, in which it was found that there was 22.2 per cent. of nitrogen

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in the total resulting volume, the quantities that had been evolved in three successive periods of examination from the beginning to the termination of the experiment were,

1st period,	21·8	per cent.	of nitrogen.
2nd ...	18·8	...	
3rd ...	26·0	...	

During the progress of this decomposition, therefore, more nitrogen relatively was evolved towards the close of the experiment than at its beginning.

From this result, therefore, I again infer that the nitrogen emitted by leaves is derived from the decomposition of some azotized body, and not from air mechanically included in their pores.

The following are the experimental results which I have obtained :—

1st. That the nitrogen comes from the tissue of the leaf itself; because more than three times as much is evolved from bicarbonate of soda as is imprisoned in the structure of the leaf, removable by the air-pump.

2nd. In twelve hours, from bicarbonate of soda, leaves will evolve more than five times their own volume of gaseous matter.

3rd. The quantity of nitrogen in the composition of leaves is sufficient for furnishing all the nitrogen obtained in the gas evolved. From Boussingault's analyses it appears that they contain nearly ten times the required amount.

4th. The decomposition of some nitrogenized constituent of the leaf is essential to the appearance of the nitrogen; there is no other available source.

At this stage of the inquiry a remarkable analogy appears between the function of digestion in animals, and the same function in plants. Liebig has shown how, from the transformation of the stomach itself, food becomes acted upon and is turned into chyme; an obscure species of fermentation brought about by the action of nitrogenized bodies. So, in like manner in plants, the decay of a nitrogenized body is intimately connected with the assimilation of carbon, for, as I have stated, the process here under discussion is a true digestion, and not a respiratory process. And as there are facts which seem to show that the primary action of the light is not upon the carbonic acid, but upon the nitrogenized ferment, the decomposition of the gas ensuing as a secondary result, *is it not probable that CHLOROPHYL is the body which in vegetables answers to the CHYLE of animals?* The oxygen, which disappears during the decomposition of carbonic acid, disappears to bring about the *eremacausis* of the nitrogenized body. And have not the gum, the starch, the lignin, and other car-

bonaceous constituents of plants, all originally existed in and passed through the green stage? It is the quality of radiant matter to determine the position of atoms and the grouping of molecules; and for this the sun, the great organizer, the great life-giver, from age to age furnishes his unfading beams. That analogies like this between the organic functions of plants and animals in reality exist we might reasonably suppose; they are agreeable to the general plan of nature.

*Note on the Tithonotype.*

In the Number of this Journal for May last, I described a process for obtaining tithonotypes, or copies of the surface of Daguerreotypes by means of gelatine.

A very important improvement on that process, an improvement which, indeed, has brought it almost at once to perfection, has been effected;—this is, *to copy the surface in copper by the Electrotype after it has been previously fixed by the agency of a film of gold.*

Those who are conversant with these matters will see at once that this is a very different thing from the abortive attempts which were made early in the history of the Daguerreotype. Many artists endeavoured to transfer its surface by precipitating copper upon it; among others I made trials of the kind. The results of those abortive attempts were mere shadowy representations which could be seen in certain lights, and which were very unsatisfactory in their effect\*.

The beautiful tithonotypes that are now so common in this city are made in the following way:—The Daguerreotype is carefully gilt by M. Fizeau's process, taking care that the film of gold is neither too thick nor too thin. The proper thickness is readily attained after a little practice. The plate is then kept a day or two, so that it may become enfilmed with air. The back and edges being varnished, copper is to be deposited upon it in the usual way, the process occupying from twelve to twenty hours. If the plate has been properly gilt, and the process conducted successfully, the tithonotype readily splits off from the Daguerreotype.

The reader will understand, that when the process succeeds the Daguerreotype will be uninjured, and the Tithonotype a perfect copy of it. If any portions are blue, or white, or flesh-coloured, they will be seen *in the same colours* in the tithonotype; the intensity of light and shadow is also given with accuracy, and indeed the copy is a *perfect copy* in all respects of the original. A great advantage is also obtained

\* Professor Grove's voltaic process for etching Daguerreotypes, has, however, produced better results than those here alluded to by Dr. Draper. See Phil. Mag. S. 3. vol. xx. p. 18.—EDIT.



in the reversal that takes place. The right side of the tithonotype corresponds to the right side of the original object, and the left to the left. In the Daguerreotype it is not so.

Copper tithonotypes were first made in this city by Mr. Endicott, a lithographic artist of distinction.

There is no great difficulty in obtaining from these tithonotypes duplicate copies. An expert artist can multiply them from one another.

The problem of multiplying the beautiful productions of M. Daguerre is therefore solved.

I will take this opportunity of making a remark which I intended to have inserted in my paper "On the rapid Detithonizing Power of certain Gases and Vapours," inserted in the March Number of this Journal (S. 3. vol. xxii.). Amateurs, in the Daguerreotype process, are often annoyed by the want of success which frequently attends them. They ascribe to the atmosphere, or to the light, or to other causes, their inability to obtain impressions. Most of these mischances are due to the accidental presence of the vapour of iodine, or other electro-negative bodies, in the chamber or about the apparatus. It is incredible what a brief exposure to these vapours will entirely destroy a picture before it is mercurialized. If the iodine box or the bromine bottle is kept in the same room with the mercury apparatus, that circumstance in itself is often sufficient to ensure an uniform want of success. If the little frame which fits into the back of the camera, and which holds the silver plate, be used in the iodizing process, as is often the case, the small quantity of vapour it absorbs will destroy every picture, or at all events increase the time required in the camera enormously. The reason of this is easily understood. Suppose a plate, in such a frame, be placed in the camera, or what comes to the same thing, suppose a particle of iodine has fallen into the camera, or that the wood has in any way absorbed an electro-negative vapour; as fast as the light makes its impression on the sensitive surface the vapour detithonizes it, and unless the light is quite intense or the exposure much prolonged, a very feeble proof, or no proof at all, will be obtained. In the same way the difficulties are greatly increased in the process of mercurialization, for the temperature resorted to being high, if there is the least particle of iodine about the box, the picture will be inevitably and instantly detithonized and ruined.

We ought therefore never to allow iodine, or bromine, or chlorine, to have access to the apartment or the apparatus in which Daguerreotype operations are being conducted.

University of New York, May 20, 1843.