



Philosophical Magazine Series 3

ISSN: 1941-5966 (Print) 1941-5974 (Online) Journal homepage: <http://www.tandfonline.com/loi/tphm14>

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To cite this article: John William Draper M.D. (1844) I. On tithonized chlorine , Philosophical Magazine Series 3, 25:163, 1-10, DOI: [10.1080/14786444408644922](https://doi.org/10.1080/14786444408644922)

To link to this article: <http://dx.doi.org/10.1080/14786444408644922>



Published online: 30 Apr 2009.



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THE
LONDON, EDINBURGH AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[THIRD SERIES.]

JULY 1844.

- I. *On Tithonized Chlorine.* By JOHN WILLIAM DRAPER, M.D., Professor of Chemistry in the University of New York.

[The following paper was read at the meeting of the British Association, held at Cork last year (1843). I have added to it, in an Appendix, some further observations subsequently made.—J. W. D.]

CHLORINE gas, which has been exposed to the daylight or to sunshine, possesses qualities which are not possessed by chlorine which has been made in the dark.

This is shown by the circumstance, that chlorine which has been exposed to the sunshine has obtained from that exposure the property of speedily uniting with hydrogen gas; a property not possessed by chlorine which has been made and kept in the dark.

This quality gained by the chlorine arises from its having absorbed tithonic rays corresponding in refrangibility to the indigo. It is not a transient, but apparently a permanent property, the rays so absorbed becoming latent, and the effect lasting for an unknown period of time. The facts which I shall proceed to describe will be interesting to chemists, because they plainly lead us to suspect that the descriptions we have of the properties of all elementary and compound bodies are either inaccurate or confused. These properties are such as bodies exhibit after they have been exposed to the light; we still require to know what are the properties they possess before exposure to such influences.

Natural philosophers will also find an interest in these phenomena, for they finally establish for the tithonic rays two important facts,—1st, that those rays are absorbed by ponderable bodies; and 2nd, that they become latent after the manner of heat. Some years ago I endeavoured to prove that

Phil. Mag. S. 3. Vol. 25. No. 163. July 1844.

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these things held for a compound substance the iodide of silver (Phil. Mag. Sept. 1841).

For reasons which will be obvious as the description proceeds, I shall speak of chlorine which has been exposed to the beams of the sun, as *tithonized chlorine*.

I. *Description of the experiment.*

In two similar white glass tubes place equal volumes of chlorine, which has been made from peroxide of manganese and muriatic acid by lamplight, and carefully screened from access of daylight. Expose one of the tubes to the full sunbeams for some minutes, or if the light be feeble, for a quarter of an hour: the chlorine which is in it becomes tithonized. Keep the other tube during this time carefully in a dark place; and now, by lamplight, add to both equal volumes of hydrogen gas. These processes are best carried on in a small porcelain or earthenware trough, filled with a saturated solution of common salt, which dissolves chlorine slowly; and to avoid explosions operate on limited quantities of the gases. Tubes that are eight inches long and half an inch in diameter will answer very well. The two tubes now contain the same gaseous mixture, and only differ in the circumstance that one is tithonized and the other not. Place them therefore side by side before a window, through which the entrance of daylight can be regulated by opening the shutter; and now, if this part of the process is conducted properly, it will be seen that the tithonized chlorine commences to unite with the hydrogen, and the salt water rises in that tube. But the untithonized chlorine shows no disposition to unite with its hydrogen, and the liquid in its tube remains motionless for a long time. Finally, as it becomes slowly tithonized by the action of the daylight impinging on it, union at last takes place. From this, therefore, we perceive that chlorine which has been exposed to the sun will unite promptly and energetically with hydrogen; but chlorine that has been made and kept in the dark shows no such property.

As I doubt not this remarkable experiment will be repeated by chemists, I will add that the only point to which attention in particular is to be given, is in the final exposure to the light. This must not be too feeble, or the action will be tedious; but the direct sunbeam must be sedulously excluded, or an explosion will result. A room illuminated by one small window, looking to the north, answers very well. It need scarcely be added that care must be taken that both tubes are illuminated alike.

II. *The change in the chlorine is not transient.*

Now it might be supposed that this apparent exaltation of the electro-negative properties of the chlorine is only a transient thing which would speedily pass away, the gas reverting to its original untithonized condition.

To show that this is not so, tithonize some chlorine in a tube as before. Place it for an hour or two in the dark along with the tube of untithonized chlorine, with which it is to be compared; then to both add hydrogen. Expose them as in the former experiment to the daylight, and the result will turn out as before, the tithonized chlorine forming muriatic acid at once, and the untithonized refusing to do so.

This, therefore, shows that the change which the sunbeams impress upon chlorine is to a certain extent a permanent change, and, unlike a calorific effect, it does not spontaneously and rapidly pass away.

III. *There are two stages in the phenomenon.*

Let us now proceed to make inquiry into the nature of the change thus impressed on the chlorine. This, I shall show, rests in the circumstance of the absorption of rays which correspond in refrangibility to the indigo, and which appear to become latent.

In a tube, over salt water, mix together equal volumes of untithonized chlorine and hydrogen gas. Expose it to the daylight, marking the time at which the exposure commences. Watch the level of the liquid in the tube narrowly, and, though stationary for a considerable time, after a certain period has elapsed it will be seen on a sudden to start and commence rising. Observe now how far it will rise during a period which is equal to the time that elapsed between the first exposure and the beginning of the rise, and it will be seen that one-fourth or half the gases will disappear.

It is obvious that from the first moment of exposure the rays must have been exerting their influences on the mixture. As will presently be proved, absorption has been all along taking place. There are, therefore, two distinct phenomena exhibited by this experiment. There is a period during which, though large quantities of the dark rays are disappearing, no visible change is produced; there is a second period, during which absorption is accompanied by a remarkable chemical effect, the production of muriatic acid. From these things we gather that a definite amount of the tithonic rays must disappear and become latent before muriatic acid can form. The phenomenon is not unlike that of the disappearance of a definite quantity of heat in the passage of ice into the condition of water.

A mixture of chlorine and hydrogen does not, therefore, instantly give rise to the production of muriatic acid on exposure to the light, but as a preliminary condition a certain definite amount of absorption must take place.

Now if this were a mere molecular disturbance, such as might be brought about by the action of heat, we should expect to find it transient and speedily passing away. Such, however, is far from being the case. As with simple chlorine, so with this mixture, after it has been tithonized it loses its quality very slowly. I have observed that after a week or more has elapsed since it was first exposed to the light, it commences to contract when placed in a feeble gleam.

IV. *Rays are absorbed in producing this change.*

I have thus far assumed that the rays which bring about these changes are absorbed; the following is the proof which I have to offer:—

Over a tube half an inch in diameter and six inches long, closed at its upper extremity and open at its lower, invert a jar of the same length and one inch and a half in diameter. Fill the tube and the jar at the salt water trough, about two-thirds full, with the same mixture of chlorine and hydrogen. Expose them to diffuse daylight. Now it is clear that no rays can gain access to the tube, except after having passed through the gaseous mixture in the jar. After a certain space of time the level of the liquid in the jar commences to rise, but that in the tube will remain much longer wholly stationary.

It therefore appears that a beam which has passed through a mixture of chlorine and hydrogen has lost, to a great extent, the quality of bringing about the union of a second portion of the mixed gases through which it may be caused to traverse. The active rays have been absorbed; they disappear from the beam, and are lost in producing their first effect.

A beam of light becomes detithonized in producing a chemical effect; the beam, as well as the medium on which it acts, becomes changed. I have a series of results which proves that this takes place for a great variety of compound bodies.

V. *It is the indigo ray which is absorbed.*

As has been said, it is a ray which corresponds in refrangibility to the indigo which produces these results.

In a small porcelain trough I inverted, side by side, ten tubes, each of which was three inches long and one-third of an inch in diameter, the trough being filled with salt water. I passed into each tube a certain quantity of untithonized chlorine and hydrogen. A beam of the sun, being directed by a heliostat into a dark room, was dispersed horizontally

by a flint glass prism, and the trough with its tubes so placed as to offer an exposure to the different coloured rays. The aperture which admitted the beam was about half an inch in diameter. For awhile no movement was observed in any of the tubes; but as soon as the preliminary absorption, previously described, was over, and the tithonization completed, the level of the liquid began to rise. In the red and in the orange no movement could be perceived, in the violet only after a time; but first of all the tube that was immersed in the indigo light was in action, and exhibited finally a very rapid rise; this was soon followed by the tube that was in the space where the indigo and violet joined, then by that in the violet, and that in the blue; the tube in the green was next in order. The following Table gives the numerical results obtained by observing the time which elapsed before movement took place in each tube:—

Table I.

Name of ray.	Time.	Name of ray.	Time.
Extreme red	*	Indigo.....	1:50
Red and orange...	+100:00	Indigo and violet..	2:00
Yellow and green.	52:00	Violet.....	2:25
Green and blue...	4:00	Violet.....	5:00
Blue	2:33	Extreme violet ...	5:50

Many years ago M. Berard made experiments on the explosion of chlorine and hydrogen, and concluded from his results that it was brought about by the violet ray. This was at a time when the methods of making these experiments were less exactly known. It is a very easy matter to prove that in reality the indigo is the active ray, and that, from a maximum point which is in the indigo, but towards the blue, the effect gradually diminishes to each end of the spectrum.

The following Table gives the calculated approximate intensity of the chemical force for each ray, deduced from the foregoing experiment:—

Table II.

Name of ray.	Force.	Name of ray.	Force.
Extreme red	Indigo	66:60
Red and orange...	1:00	Indigo and violet..	50:00
Yellow and green.	1:90	Violet.....	44:40
Green and blue ...	25:00	Violet.....	20:00
Blue	42:90	Extreme violet ...	18:10

* Even after the longest exposure I had the means of giving it, no movement took place in the tube which was in the extreme red, and I am doubtful about that in the red and orange.

There is a great advantage which experiments conducted in this way possess over those which depend for their indication on the stains impressed on Daguerreotype plates or sensitive papers. In those cases we obtain merely a comparative contrast for different regions of the spectrum; in this we have absolute measures determined by a definite chemical effect and the rise of a liquid in a graduated tube; and from this we gain juster views of the true constitution of the spectrum. On studying the numbers in the foregoing table, or better still, if we project them, it will appear what an enormous difference there is in the chemical force of the different rays. In the experiment from which I have deduced this table, it appears that the force of the indigo ray exceeds that of the orange in a greater ratio than 66 to 1; and from the circumstances under which the experiment is made, this difference must be greatly underrated. There is always diffused light in the room coming from the introritted beam, and this accelerates the rise in the less refrangible tubes; then again, it is impossible that the tube which gives the greatest elevation shall coincide mathematically with the maximum point and express the maximum effect.

From some estimates I have made, I am led to believe that in point of chemical force, for this mixture of chlorine and hydrogen, the indigo ray exceeds the red in a higher ratio than 500 to 1.

VI. *The action is positive from end to end of the spectrum.*

M. Becquerel found, that for a Daguerreotype plate the red, the orange, and the yellow rays possess the quality of continuing the action begun by the more refrangible colours; he therefore names these "*rayons continueurs*." For the same compound I found that those rays, acting horizontally with the diffused daylight, exerted a negative agency. It is therefore desirable to understand whether, with respect to the gases now under consideration, the lesser refrangible rays exert anything in the way of an action of depression or hindrance to union. By direct experiment I found that this was not the case, the action being positive from end to end of the spectrum. This can be shown by removing the tubes, after they have been in the spectrum for an hour or two, into the gleams of daylight. One by one they exhibit after a time a rise, the order being the green first, then the yellow and the orange, and at last the red. And if at the same time a tube which has been kept in the dark be exposed along with them, they will all rise before it, showing that tithonization had set in and been going on in them all; that it had been more active

in the green than in the yellow, in the yellow than in the orange, in the orange than in the red; and, had the exposure to the spectrum been long enough, the liquid in every one of the tubes would have risen.

VII. *The indigo ray forms the muriatic acid as well as produces the preliminary tithonization.*

It only now remains to inquire, whether the rays which cause the production of the muriatic acid are those which effect the tithonization of the chlorine; in other words, whether the first stage of the process is brought about by the same agent which carries on the second. The experiment which I have just described shows that tithonization is most actively produced by the indigo ray, and it is easy to show that it is the same ray which carries on the second part of the process; for, if before placing the tubes in the prismatic spectrum we tithonize them in the daylight, so that the liquid has just commenced to rise in each, and then expose them to the spectrum, it will be found that the tube in the indigo rises most rapidly, and the others in the order stated before. Therefore we perceive that the same ray commences, carries on, and completes the process.

Few substances can exceed in sensitiveness to light a mixture of chlorine and hydrogen previously tithonized. Brought into the obscure daylight of a gloomy chamber, it is remarkable how promptly the level of the liquid in the tube rises; how, when the shutters are successively thrown open, the action becomes more and more energetic; and how, in an instant, it stops when the instrument is shaded by a screen.

I have not recorded in this communication a multitude of experiments of detail which go to support the conclusions here drawn, and which will be published at a proper time. It has been my object on this occasion to call attention to the fact, that chlorine, an elementary body, undergoes a change after exposure to the light; a change which appears to produce an exaltation of its electro-negative properties, as is shown by its power of uniting more energetically with hydrogen. This change must not be confounded with those transient elevations of activity due to increased temperature, inasmuch as this is more permanent in its character. It arises from the absorption of rays which exist most abundantly in the indigo space of the spectrum. That the phænomenon is due to a true absorption is fully shown in the circumstance, that a beam which has produced this effect has lost the quality of ever after producing a similar result. This is borne out by what we ob-

serve to take place when a feeble light falls on a mixture of chlorine and hydrogen which has been prepared in the dark. A certain space of time elapses before any formation of muriatic acid occurs, during which the absorption in question is going on; and when that is completed, and the mixture is tithonized, union of the gases begins and muriatic acid forms. From end to end of the spectrum the action is positive, and differs only in intensity; but this difference in intensity opens before us new views of the constitution and character of the solar beam.

University of New York,
June 20, 1843.

The foregoing paper was written almost a year ago, and since that time I have made several new observations corroborative of the results given.

Chlorine is not the only elementary substance in which the rays produce a change. In his chapter on phosphorus, Berzelius remarks, "Light produces in it (phosphorus) a peculiar change, of which the intimate nature is unknown; and which, so far as we can judge at present, does not alter its weight. It makes it take a red tint. This phenomenon occurs not only in a vacuum, even in that of a barometer, but also in nitrogen gas, in carburetted hydrogen, under water, alcohol, oil and other liquids. When we expose to the sunlight phosphorus dissolved in æther, oil, or hydrogen gas, it instantly separates under the form of red phosphorus; it undergoes very rapidly this modification in *violet light*, or in glass vessels of a violet colour. The light of the sun makes it easily enter into fusion in nitrogen gas, but it does not melt in hydrogen, and in the Torricellian vacuum it sublimes in the form of brilliant red scales." (Berzelius, *Traité*, tom. i. p. 258.)

Again, when speaking of phosphuretted hydrogen, he says, "Exposed to the influences of the direct solar light this gas is decomposed, a part of the phosphorus separates under the form of red phosphorus, and is deposited on the interior surface of the glass. If we cover the vessel which contains the gas imperfectly, no phosphorus is deposited on the covered spaces." (Ib. tom. i. p. 265.)

As Berzelius does not give these experiments as his own, and I do not know to whom we are indebted for them, I repeated some of them. Among other corroborative results, it appeared, that a piece of phosphorus of a pale or whitish colour, in a vessel filled with pure and dry carbonic acid gas, placed in the sunshine, rapidly exhibited the phenomenon in question. Eventually the phosphorus became of a deep blood-

red colour, and on the sides of the glass towards the light, feathery crystals formed, the tint of which bore a close resemblance to that of the red prussiate of potash.

Since the invention of the tithonometer, I have been able to observe more closely the habitudes of chlorine. In the description given of that instrument in the December number (1843) of this *Journal*, it is recommended to cast aside the first observation, because it never gives an accurate estimate of the true effect. When a mixture of chlorine and hydrogen is exposed, muriatic acid does not immediately form; but a preliminary tithonization is necessary, and then at the end of a certain period contraction begins to take place.

A tithonometer exposed to the daylight is much too powerfully affected to allow of the successive stages of change to be distinctly made out; the preliminary tithonization is accomplished so rapidly, that the indications of it are merged and lost in the contraction which instantly follows. It is necessary therefore that we should operate with a *small* lamp-flame.

To such a flame I exposed a mixture of chlorine and hydrogen, and marked the number of seconds which elapsed before contraction, arising from the production of muriatic acid, took place. The first indications of movement occurred at the close of 600 seconds.

The index then moved through the first degree in 480 seconds

...	second	...	165	...
...	third	...	130	...
...	fourth	...	95	...
...	fifth	...	93	...
...	sixth	...	93	...

and continued to move with regularity at the same rate.

These observations, therefore, prove that a very large amount of radiant matter is absorbed before chemical combination takes place; and that in the case of chlorine and hydrogen the total action is divisible into two periods; the first during which a simple absorption is taking place without a chemical effect, the second during which absorption is attended with the production of muriatic acid.

The facts which I am endeavouring to set forth prominently in this communication are,—1st, the preliminary tithonization just discussed; and 2nd, the persistent character of the change impressed upon chlorine when it has been exposed to the sun, an effect wholly unlike a calorific effect, which would soon disappear.

By resorting to the tithonometer we obtain information equally distinct upon the second point, that the preliminary

tithonization is not a transient effect which at once passes away, but is, on the contrary, a persistent change.

I tithonized the chlorine and hydrogen contained in the instrument, and kept it in the dark for ten hours. On exposure to the lamp rays it moved after a few seconds, showing, therefore, that the change which had been impressed on the chlorine was not lost. In the former case 600 seconds had elapsed before any movement was visible.

When, however, we remember that the invisible images on Daguerreotype plates, and even photographic impressions on surfaces of resin, and probably all other similar changes are slowly effaced, it would be premature to conclude that tithonized chlorine does not revert to its original condition. I have sometimes thought that there were in several of my experiments indications that this was taking place, but would not be understood to assert it positively. Whether it be so or not, one thing is certain, that the taking on of this condition and the loss of it is a very different affair from any transient exaltation of action due to a temporary elevation of temperature, or the contrary effect produced by cooling.

April 26, 1844.

II. *On Quaternions; or on a new System of Imaginaries in Algebra**. By Sir WILLIAM ROWAN HAMILTON, LL.D., P.R.I.A., F.R.A.S., Hon. M. R. Soc. Ed. and Dub., Hon. or Corr. M. of the Royal or Imperial Academies of St. Petersburg, Berlin, Turin, and Paris, Member of the American Academy of Arts and Sciences, and of other Scientific Societies at Home and Abroad, Andrews' Prof. of Astronomy in the University of Dublin, and Royal Astronomer of Ireland.

1. LET an expression of the form

$$Q = w + ix + jy + kz$$

be called a *quaternion*, when w, x, y, z , which we shall call the four *constituents* of the quaternion Q , denote any real quantities, positive or negative or null, but i, j, k are symbols of three imaginary quantities, which we shall call *imaginary units*, and shall suppose to be unconnected by any linear relation with each other; in such a manner that if there be another expression of the same form,

$$Q' = w' + ix' + jy' + kz'$$

the supposition of an equality between these two quaternions,

$$Q = Q',$$

* A communication, substantially the same with that here published, was made by the present writer to the Royal Irish Academy, at the first meeting of that body after the last summer recess, in November 1843.