

## **The early history of chlorine / papers by Carl Wilhelm Scheele ... [and others].**

### **Contributors**

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THE EARLY HISTORY  
OF  
CHLORINE.

PAPERS BY

CARL WILHELM SCHEELE

(1774).

C. L. BERTHOLLET

(1785).

GUYTON DE MORVEAU

(1787).

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(1809).

Alcembic Club Reprints,  
No. 13.



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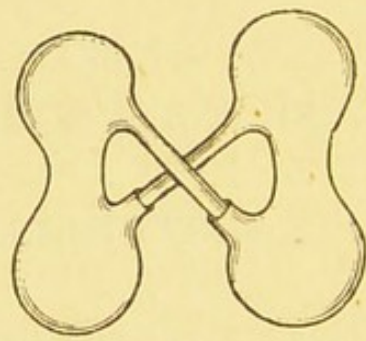
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## PREFACE.

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THE history of chlorine forms one of the most interesting and important chapters in the whole of chemistry, and this collection of papers is issued in order that students may have access to all the important early work on the subject. The volume containing Davy's researches (Reprint No. 9) may be taken as a continuation of the present one.

The first paper contains Scheele's description of the discovery of chlorine, made accidentally when he was investigating the properties of "Brunsten" (black oxide of manganese). It is interesting to note, not only his clear and wonderfully correct views as to the nature of the substance, but also the very full description of it which he gives in a small space.

In marked contrast to the preceding one is the long paper by Berthollet, in which, carried away by his zeal for Lavoisier's doctrines, he propounds the view that chlorine is the higher oxide of an as yet unknown radical. This view, although founded so loosely, obtained general adoption, and became so firmly rooted that it was only given up after one of the fiercest controversies connected with the science.

The extract from de Morveau's Memoir is reprinted simply to shew clearly the position of chemists at that time. Although not directly connected with the matter



in hand, it is perhaps permissible to call the attention of any chemists who use the expression "radicle" to the historical authority for "radical" contained in the second paragraph of the extract.

The extracts from Gay-Lussac and Thenard bring us to the time of Davy. These three investigators were simultaneously engaged in investigating the properties of chlorine and hydrochloric acid, and endeavouring to isolate the radical. Before long, Davy concluded that chlorine contained no oxygen, but was itself an element; this view was not adopted by his rivals till considerably later. Nevertheless, it is sometimes claimed that Gay-Lussac and Thenard first established the elementary nature of chlorine. This claim is apparently founded on the statement at the end of the paper now reprinted (p. 48). That it is not justified is clearly shewn by the extract from their "Physico-chemical Researches" given at the end of the present volume.

As in the other translations of the Alembic Club Reprints, the endeavour has been to give a fairly accurate reproduction of the author's language rather than an elegant version.

H. M.

# ON MANGANESE,

*And its Properties.*

BY CARL WILHELM SCHEELE.\*

\* \* \* \* \*

*Behaviour of Manganese with common Marine Acid.*

6. (a) One ounce of pure *spiritus salis* was poured on half an ounce of finely-ground manganese. After this mixture had stood one hour in the cold, the acid had assumed a dark brown colour. Part of this solution was poured into a bottle, which was left open in a warm place. The solution gave off a smell like warm *aqua regis*, and after a quarter of an hour it was clear and colourless as water, and the smell was gone. (b) The remainder of the brown mixture was set to digest, in order to see whether the marine acid would saturate itself with manganese. As soon as the mixture became warm, its smell of *aqua regis* became considerably augmented, and an effervescence also arose, which continued till the following day, when the acid was found to be saturated. On the residue which it had been unable to dissolve, there was again poured one ounce of *spiritus salis*, whereupon all the above-mentioned phenomena occurred, and the manganese became completely dissolved, except a little siliceous earth.

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23. The sixth paragraph shews the behaviour of manganese with marine acid. In this case it is not so easy

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\* [Translated from "Om Brunsten, eller Magnesia, och dess Egenskaper," Kong. Vetenskaps Academiens Handlingar, xxxv., pp. 89, 93, 94, 105-110. Stockholm, 1774.]

to understand at first whence the manganese has obtained its phlogiston; nothing combustible is added here, and nevertheless the complete dissolution of the manganese can be effected without heat. In fact, there occurs here a phenomenon which proves that phlogiston is certainly present in marine acid—a property which one would have attributed to nitrous acid, since chemists, subsequent to STAHL, have believed that this principle is required in considerable quantity as one of its constituents. That, however, we may now reverse and attribute to marine acid.

When marine acid stood over manganese in the cold it acquired a dark reddish brown colour (§ 6, *a*). As manganese does not give any colourless solution without uniting with phlogiston, it follows that marine acid can dissolve it without this principle. But such a solution has a blue or a red colour (§ 14, No. 4). The colour is here more brown than red, the reason being that the very finest portions of the manganese, which do not sink so easily, swim in the red solution; for without these fine particles the solution is red, and red mixed with black makes brown. The manganese has here attached itself so loosely to *acidum salis* that water can precipitate it, and this precipitate behaves like ordinary manganese. When, now, the mixture of manganese and *spiritus salis* was set to digest, there arose an effervescence and smell of *aqua regis* (§ 6, *b*).

In order clearly to apprehend this novelty I took a retort containing a mixture of manganese and *acidum salis*. In front of the neck I bound a bladder emptied of air,\* and set the retort in hot sand. The bladder became distended by the effervescence in the retort. When the acid no longer effervesced, which was an indication of its saturation, I removed the bladder, and

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\* [Compare Alembic Club Reprint, No. 8, § 30.]

found that this air had coloured it yellow, as if by *aqua fortis*, but did not contain any trace of *aer fixus*; it had, however, a quite characteristically suffocating smell, which was most oppressive to the lungs. It resembled the smell of warm *aqua regis*. The solution in the retort was clear, inclining to yellow, which last mentioned colour was caused by its containing iron. If one wishes to be convinced that this dissolved manganese contains phlogiston, let him precipitate the solution with *alkali tartari*, edulcorate the precipitate, and then proceed therewith as is described in § 15, *a, b, c*. But whence has this manganese obtained phlogiston? From *acidum salis*. Here we cannot have recourse to heat, because the solution becomes clear without it, only it must stand several hours in the open air. What happens to the solution is as follows: The manganese is first attracted by the marine acid, whence a brown solution arises. By the help of the acid this dissolved manganese acquires a strong attraction for phlogiston (§ 14, No. 2), and actually draws it to itself from the particles of acid with which it is united. This part of the acid, which has thus lost one of its constituents and is only very loosely united to the now more phlogisticated manganese, is driven out from its earth by the remaining marine acid which has not yet suffered any decomposition, and appears then, with effervescence, as a highly elastic air, or similar fluid; the brown colour has then disappeared and a water-clear solution resulted.

24. This marine acid, deprived of phlogiston as one of its constituents, unites with water in very small quantity; and gives the water a slightly acid taste; but as soon as it comes in contact with a combustible matter it becomes again a proper marine acid. In order to investigate the properties of this air it is best to put it to the test in the elastic state. Ordinary marine acid

is mixed with finely-ground manganese, in any chosen quantity, in a glass retort which is placed on warm sand; small bottles which hold about twelve ounces of water are employed as receivers; about two drachms of water are put into each bottle, and the joints are not luted except by means of grey paper wrapped round the neck of the retort, and on this the bottle is fixed. When a bottle has remained a quarter of an hour or more, it is found, according to the quantity of the elastic acid in the receiver, that the air in it assumes a yellow colour; the bottle is then removed from the retort.

If the paper luting has held tight, a part of the air escapes with force; a previously fitted cork is then immediately inserted into the bottle, and another bottle is fixed to the neck of the retort in its stead. In this way several bottles can be partly filled with dephlogisticated marine acid. It is to be noted that the retort must be placed in such a position that in case drops should rise into the neck they can flow back. The water in the bottles serves this purpose, that, should any vapour of muriatic acid pass over, it may have this water to which it may betake itself. I take more than one bottle so that it is not necessary for me to start a new distillation for each experiment that I make. It is not advantageous to fill large globes, as a good deal of the acid escapes into the air every time they are opened.

25. Whatever was experimented with in this dephlogisticated marine acid was hung on a glass tube which I fastened into the cork. (a) The corks in the bottles became yellow, as from *aqua fortis*, and during the distillation the luting was likewise attacked. (b) Blue litmus paper became almost white; all vegetable flowers—red, blue, and yellow—became white in a short time; the same thing also occurred with green plants. In the meantime the water in the bottle became changed to a

weak and pure marine acid. (c) The former colours of these flowers, as well as those of the green plants, could not be restored either by alkalies or by acids. (d) Expressed oils and animal fats, when they hung as drops on the glass tube or were rubbed on it, became in a short time tough like turpentine. (e) Cinnabar became white on the surface, and when the piece was washed in water a pure *mercurius sublimatus* solution was obtained, but the sulphur was not altered. (f) Iron vitriol became red, and deliquesced. Copper and zinc vitriols were unaltered. (g) Iron filings were put into the same bottle and they dissolved. This solution was evaporated *ad siccum* and distilled with addition of oil of vitriol, when a pure marine acid, which did not dissolve gold, again passed over. (h) All metals were attacked, and with gold it is noteworthy that its solution in this dephlogisticated marine acid forms with *alkali volatile* an *aurum fulminans*. (i) When *spiritus salis ammoniaci*, prepared with lime, hung in drops on the tube, there arose a white cloud, and a quantity of air bubbles escaped from the drops, which gave off a smoke when they burst asunder. (k) *Alkali fixum* was changed into *sal commune* which decrepitated on charcoal, but did not detonate. (l) Arsenic deliquesced in these vapours: (m) Insects immediately died in them; (n) and fire was immediately extinguished by them.

26. This proves sufficiently the great attraction which dephlogisticated marine acid has for the combustible.\* It is possible that STAHL obtained such a dephlogisticated marine acid by means of iron, as he concludes from the yellow colour on the cork, and imagined that the marine acid was changed into nitrous acid. If a mixture of

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\* [“Den brenbara” might be translated “phlogiston;” but Scheele also uses the latter word, so the literal translation is adopted here.]

manganese, *spiritus salis* or *spiritus vitrioli*, and *alcohol vini* is digested several days in a well-closed flask, and thereafter gently distilled, there arises no effervescence, but *spiritus vini* passes over; it has, however, and this is noteworthy, a strong smell of *aether nitri*. The residue in the retort has lost its acid, and is saturated with manganese. If metals, sugar, turpentine, or linseed oil are added to a mixture of ground manganese and marine acid there arises no dephlogisticated marine acid; for here there is sufficient combustible present with which this elastic acid can combine. With mercury it is noteworthy that a good deal of it also goes into the solution, from which it can be obtained by crystallisation, and behaves like corrosive sublimate. If leaves of pure gold are put into a mixture of ground manganese and pure *acidum salis*, it is found afterwards that this solution contains gold, as well as manganese, dissolved.

# MEMOIR

## *On Dephlogisticated Marine Acid.*

By M. BERTHOLLET.\*

The important experiments by which the nature of water had just been determined, and the happy application which M. DE LA PLACE had made of them to the production of inflammable gas by the dissolution of metals, threw great light on the whole of chemistry; phlogiston, that principle which STAHL had ingeniously imagined in order to account for a large number of phenomena, and by means of which there was really established between them a connection which has served for a long time to guide chemists in their researches, appeared to me to have at last become a useless hypothesis, whereupon I believed it incumbent on me to subject dephlogisticated marine acid to new experiments, as its properties might destroy or confirm the opinion I had adopted. These experiments were the subject of a memoir which I read at the public meeting of 6th April 1785. I shall now enter into greater detail, add some new observations, and reply to some objections which have since then been made to the theory which I had established.

SCHEELE, when investigating the effects which different acids produced on manganese, observed that muriatic acid produced an effervescence with it, and that there

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\* [Translated from "Memoires de l'Académie Royale" for the year 1785. Pp. 276-295. Paris, 1788.]



was disengaged a vapour similar to that from hot aqua regia. He says, "The manganese is first attracted by the muriatic acid, thereafter it acquires, by means of the acid, a stronger affinity for phlogiston, and then it abstracts the latter from the particles of the acid with which it has not itself combined. This portion, thus deprived of one of its constituent parts and feebly united to the phlogisticated manganese, is sublimed by the rest of the acid which is still undecomposed, and manifests itself, with effervescence, as a very elastic air or as a fluid resembling air.

Muriatic acid deprived of phlogiston, which is in one of its constituent parts, only unites with water in very small quantity and does not render it strongly acid, but as soon as it meets with a phlogisticated substance it becomes again a true muriatic acid. It is in its elastic state that the qualities of this air are best shewn."

He thereafter describes how this vapour ought to be collected in small flasks which are adapted to the neck of the retort, and in which a little water has been placed.

BERGMAN adopted SCHEELE'S view; with him he regards manganese as a substance very avid of phlogiston, and believes that it removes this principle from the marine acid, which thereby acquires the properties characterising the gas of dephlogisticated marine acid, and that this gas acts upon substances which contain phlogiston by removing this principle from them. It is to these two illustrious chemists that we owed the chief and almost the only ideas which we had about dephlogisticated marine acid when I turned my attention to it.

I commenced by assuring myself that dephlogisticated marine acid, in the form of gas, combined with water more easily and more abundantly than acid of chalk. After that, I tried to saturate water with it in the least embarrassing manner and without exposing myself to

breathing it, for it is suffocating. SCHEELE in his experiments employed one part of manganese to two of marine acid; but I have found that one part of manganese to four parts of fuming marine acid, or to six of ordinary marine acid, is sufficient, and even that in these proportions there is a fairly considerable portion of manganese which is not attacked by the marine acid. I pour the marine acid on the pulverised manganese contained in a tubulated retort to which I have previously adapted an empty bottle, and, successively, in the manner of M. WOULF, three other bottles almost filled with water; the last bottle communicates by a tube with a vessel which is filled with water, and on which, when the air of the apparatus is expelled and the smell of dephlogisticated marine acid begins to be perceptible, I invert a large bottle likewise full of water.

If I employ fuming marine acid the gas begins to come off in abundance without the necessity of applying heat to the retort, but if the marine acid is of only medium strength I put a slight fire below the retort from the commencement, and augment it gradually until the liquid enters into ebullition; shortly after the ebullition has commenced, the operation comes to an end; its termination is announced by the drops of marine acid which fall from the beak of the retort into the first bottle.

As absorption proceeds, the water assumes a greenish yellow colour, and when it approaches saturation the gas assumes a concrete form; in this state it gradually descends to the bottom of the liquid in small yellowish flakes, so that its specific gravity is a little greater than that of the saturated water; but, to obtain it in this form, it is necessary that the temperature of the place where the experiment is performed should not be too far from the freezing point, and further, the bottles should be surrounded by pounded ice, or, if they are relatively

too large, it may even be necessary to saturate the liquid by a second operation. Each ounce of marine acid employed suffices to saturate about a pint of water. In a second operation the water contained in the inverted bottle, which has absorbed that portion of the gas which could not enter into combination in the bottles of the apparatus, may be employed for filling these; by this means there is no loss of the gas, and breathing it is avoided.

The concrete form of dephlogisticated marine acid resumes the gaseous state when it is exposed to a feeble degree of heat; if the hand is placed upon the bottom of the bottle which contains it, it is seen to resolve itself into bubbles which rise to the surface; hence it is difficult to preserve it in closed vessels; a part, however, dissolves again in the liquid. It is chiefly in the liquid state that I have examined dephlogisticated marine acid; to determine its specific gravity I decanted the liquid from the concrete part, the thermometer being at 5 degrees above zero, and I found it to be 1003. It has a harsh taste which does not resemble that of the acids. SCHEELE and BERGMAN have observed that it destroyed vegetable colours; and it produced this effect, which I shall analyse further on, more or less promptly without any red tint becoming perceptible. A property which specially merits attention is that it does not cause an effervescence with solution of fixed alkali even when the latter is saturated with fixed air. The fixed alkalies, nevertheless, contract an affinity, and combine with it; for they cause it to lose its colour and a great part of its odour, as lime also does. If, after having added the alkali, acetous acid is poured into it, an effervescence is seen to be immediately produced, as if the alkali were simply dissolved in the water, and the odour regains all its sharpness.

The calcareous earth, when it is in the effervescent state,

has also the property of combining with dephlogisticated marine acid, and dissolves in it in fairly considerable quantity; it is precipitated from it by all the alkalies, and even by lime water; which proves that lime combines with this liquid more strongly than effervescent calcareous earth does.

We can therefore, as it seems to me, regard dephlogisticated marine acid as almost entirely deprived of acidity. SCHEELE and BERGMAN were unable to recognise this essential property, as in the process which they employed the water of the vessels in which they received the gas could contain only a very small portion of dephlogisticated marine acid, mixed with a portion of marine acid which always passes over in the distillation; in my apparatus this portion of marine acid is retained in the first bottle, which I leave empty, and which it is well to surround with ice or cold water. When the operation is not made with sufficient care a little marine acid passes even into the first bottle which is filled with water; this accident can be easily recognised by pouring into the liquid some solution of effervescing fixed alkali; if any bubbles are seen to be disengaged this is a proof that it contains some marine acid, for it should not produce any effervescence.

In a retort at the pneumato-chemical apparatus, I boiled a mixture of mineral alkali and dephlogisticated marine acid; much gas was disengaged, of which a great part was fixed air, and the other part at first atmospheric air and then air purer than this, but the last portions were hardly anything but fixed air. With lime there is no fixed air disengaged, but atmospheric air which gradually approaches to vital air, and finally a little very pure vital air. The fixed air of the first experiment is thus furnished by the alkali, as it is in the effervescences, the atmospheric air is due to the space which I left empty in the apparatus, and the vital air to the dephlogisticated marine acid.

The salt which is found in the retort is similar to sea salt, which explains the observation of SCHEELE and BERGMAN as to the identity of the neutral salts formed by dephlogisticated marine acid with those of ordinary marine acid. They were obliged to suppose that the alkalies imparted some phlogiston to the dephlogisticated marine acid and that too without themselves suffering any alteration in their properties by this loss.

I calcined some manganese at a strong heat in a pneumato-chemical apparatus. I extracted from it, as had already been observed, a large quantity of vital air; it lost an eighth of its weight. In this state I treated it with marine acid and obtained from it a much smaller quantity of dephlogisticated marine acid.

It is therefore to the vital air of the manganese, which combines with the marine acid, that the formation of the dephlogisticated marine acid is due. I ought to state that this theory was presented and announced some time ago by M. LAVOISIER, and that M. DE FOURCROY has made use of it in his Elements of Chemistry and Natural History to explain the properties of dephlogisticated marine acid such as they were then known.

The experiments which I have just described have not appeared sufficiently conclusive to some chemists; I shall take from the first part of the learned Dictionary of Chemistry, which M. de MORVEAU has just published, the reasons which can be adduced to prove the necessity of phlogiston in the explanation of the properties of dephlogisticated marine acid. I reduce to three the objections of this celebrated chemist: 1.° marine acid does not combine with vital air in the elastic state, how could it remove it from a substance by a simple affinity? 2.° when dephlogisticated marine acid combines with the alkalies, the earths, or the metals, there is nothing to prove that it does not receive phlogiston or inflammable

gas from them in exchange; *for this fluid*, according to M. de MORVEAU, *is nothing but phlogiston itself brought into the state of gas by the matter of heat*; 3.° the differences which manganese presents in the states of regulus, of white calx, and of black calx, and the effects which it produces when it is treated before the blow-pipe or when it is mixed with other substances can only be explained by means of phlogiston.

But, 1.° the elastic state of a fluid is an obstacle to combination, whatever may be the cause which holds the parts of the fluid in expansion; this is a general fact, for the explanation of which phlogiston is of no service, for, at a low temperature, vital air cannot combine with inflammable gas in the elastic state, although, according to M. DE MORVEAU, inflammable gas is nothing but phlogiston, and vital air has a great affinity for it. If, then, we do not go back to the cause of the elasticity of fluids, the difficulty is no less great in following the opinion of M. DE MORVEAU; but if we regard vital air as a compound of the principle of light or of heat with a base, as experiments prove, there remains much less obscurity for those who reject the theory of phlogiston. In fact, a substance must be in a state to overcome the affinity which the principle of light has for the base of vital air, in order to expel the former, and form with the latter a new compound; but marine acid has a very feeble affinity for vital air, it cannot combine with it except by compound affinities, and easily gives it up to all substances with which this principle has any affinity. There will be found at the end of this memoir explanations regarding the third objection.

2.° I saturated distilled water with dephlogisticated marine acid, but although I repeated the operation three times, and the bottle was well surrounded with ice, I could not obtain any in the concrete form, because the

thermometer was at 18 degrees. With this liquid I filled a bottle communicating by means of a tube with a pneumato-chemical apparatus; this bottle with the tube, which was itself filled with the liquid, was of the capacity of 51.1 cubic inches; I exposed it to sunlight; I soon saw a large quantity of small bubbles become disengaged, which, on being collected in a bottle filled with water, formed at the end of several days a volume of air of 15.27 cubic inches, the thermometer being at 17 degrees. The dephlogisticated marine acid lost its colour gradually; in this state the liquid no longer destroys blue vegetable colours but reddens them strongly, like ordinary marine acid; it produces an effervescence with fixed alkalies; it retains an odour of dephlogisticated marine acid which is scarcely perceptible; in fine, it is reduced almost entirely to ordinary marine acid.

To determine the quantity of this acid which was present in the liquid, I precipitated it by a solution of silver, and, with the same solution, I also precipitated 500 grains of marine acid, of which the specific gravity was to that of distilled water as 1141 is to 1000, and which I had diluted with distilled water. The two precipitates were dried equally; the 500 grains of marine acid gave 7 gros 43 grains of muriate of silver, and the dephlogisticated marine acid gave 5 gros 23 grains, so that, neglecting the volume of liquid which was put into the tube, 50.45 cubic inches of dephlogisticated marine acid contained 350.09 grains of marine acid of a specific gravity equal to that of the 500 grains employed, which comes to about 7 grains per cubic inch of liquid.

The air which was disengaged from the dephlogisticated marine acid having been put over a solution of liver of sulphur, was absorbed, leaving a residue of one cubic inch, so that it consisted of vital air, which contained one-fifteenth of mephitic air, the latter being without doubt due

to some atmospheric air which would be disengaged both from the water and from the apparatus which I employed. I do not deduct its volume, however, because there remained a small portion of dephlogisticated marine acid which had resisted decomposition, and because the water was impregnated with vital air, so much so, that on agitating it, bubbles escaped from it; there would rather be a small addition to make.

Accordingly 51.1 cubic inches of liquid contained 15.27 cubic inches of vital air, at the temperature of 17 degrees, which makes about 0.299 cubic inch of vital air per cubic inch of liquid; but I need not state that in these calculations I do not profess to give anything but approximations.

In an experiment made with dephlogisticated marine acid which had been obtained at a lower temperature, and which had been decanted from a concrete portion, I found that the liquid contained about a quarter less of acid and of vital air; so that dephlogisticated marine acid follows in its combination with water, a law different from that followed by the other elastic fluids which can combine with it, which unite with it in greater quantity the more the temperature approaches the freezing point: this arises from the tendency of dephlogisticated marine acid gas to take the concrete form by means of cold; but this difference is limited within a very small compass, for as soon as the thermometer is some degrees above freezing point, dephlogisticated marine acid tends to separate from the water and resume the elastic state. Hence it appears that the best way to obtain this liquid very concentrated is to produce in it a fairly considerable quantity of concrete substance, and then to let this dissolve at a temperature approaching the 10th degree of REAUMUR's thermometer; it is also at about this degree of heat that we can obtain the greatest effects of the liquid



on the substances which are submitted to its action; and on applying heat this effect is diminished by the tendency towards the gaseous state which is communicated to the dephlogisticated marine acid. This consideration may also apply to various other chemical solutions, and serves to explain the interesting observation of M. DE BUTINI, who noticed that aerated water dissolved so much the more magnesia the colder it was.

These experiments ought to dispel any doubts which might remain as to the nature of dephlogisticated marine acid; the latter is manifestly formed by the combination of vital air with marine acid, but in it the vital air is deprived of a part of the principle of elasticity, and adheres so feebly to the marine acid that the action of light suffices to disengage it promptly, light having more affinity for its base than marine acid has. There are, then, two conditions which dispose it to quit the marine acid in order to combine with substances with which it has affinity, and which render dephlogisticated marine acid proper to discover what are the properties which depend on combination with vital air, which could not have taken place except by more complicated or much slower means. It is vital air, then, which disguises the properties of dephlogisticated marine acid; it loses them as soon as that principle separates from it.

Dephlogisticated marine acid dissolves iron and zinc without any gas being disengaged, and in the same manner as water dissolves salt; for that these metals should dissolve in an acid it is only necessary that they should unite with a portion of vital air, as M. LAVOISIER has proved; and as dephlogisticated marine acid can furnish them with the portion of vital air necessary when it dissolves them, there is no decomposition of water and no inflammable air is produced.

But, if one is inclined to suppose that light gives

phlogiston to the dephlogisticated marine acid which is exposed to it, let us see what are the consequences which would follow therefrom. Firstly, it would require that the light should give phlogiston to dephlogisticated marine acid without communicating any to vital air, with which, however, it is believed that it has a very great affinity; secondly, as phlogiston is no other than inflammable gas, according to Messrs KIRWAN, DE MORVEAU, DE LA METHERIE, and some other chemists, it must be supposed that light contains a large quantity of inflammable gas and that the sun every instant suffers an immense loss of matter. Will one say that iron and zinc contain inflammable gas which they give to dephlogisticated marine acid whilst they combine with its vital air? The difficulty remains unaltered, for light would have to be able to decompose dephlogisticated marine acid just the same. If now, physicists cannot admit that light gives inflammable gas, I say that it would be proved by the experiment of which I have just spoken that iron and zinc do not contain inflammable gas, even although the direct experiments which have been made on this subject should not be decisive. Finally, chemists agree that the metals are reduced to calces when they are dissolved by means of marine acid, and consequently that they are combined with vital air; but it is not the marine acid which has been able to communicate the vital air to them, for it is not decomposed in these dissolutions; it must necessarily be the water then which furnishes it to them, as it must be it which gives the inflammable gas, as M. DE LA PLACE has shewn: these truths lend a mutual support.

When solution of mercurial nitre is poured into dephlogisticated marine acid no white precipitate is produced; but on evaporating the liquid, corrosive sublimate is obtained from it. Similarly, if white precipitate is put into dephlogisticated marine acid it dissolves, the

odour and the colour of the dephlogisticated marine acid disappear, vegetable colours are no longer destroyed, and the marine acid is meanwhile in combination; for, on adding to the liquid a little lime water, there is immediately formed a mercurial precipitate, which would not take place if a portion of marine acid were free. Hence it results that the difference between white precipitate and corrosive sublimate consists in this, that in the latter the mercury is combined with a greater quantity of vital air and marine acid.

The manner in which dephlogisticated marine acid acts on mercury merits attention; if some of this liquid is put on a certain quantity of mercury, the surface of the metal blackens, there is formed the calx of mercury known by the name of *ethiops per se*, and the liquid reddens blue paper, so that the metal begins by removing the vital air from the marine acid. If they are still left in contact the calx of mercury which has been formed takes up marine acid and becomes white, it passes into the state of combination known by the name of *panacea*, and the supernatant water does not contain either acid or mercurial salt; if it be poured off and dephlogisticated marine acid anew added, there is at once formed a combination with the mercurial salt, which, according to the quantities of marine acid which it absorbs, takes successively the properties of *mercurius dulcis* and of white precipitate, and then, if the liquid is renewed, it dissolves and forms corrosive sublimate; so that in this experiment the whole series of mercurial muriates is obtained, to which corresponds that of their causticity.

SCHEELE announced that dephlogisticated marine acid had no action on sulphur, but M. DE MORVEAU has ascertained that it changes it into vitriolic acid. When some is poured on a small portion of solution of hepar made with fixed alkali, there is no hepatic gas disengaged

and there is only very little precipitate formed; the odour of the dephlogisticated marine acid is dispelled, and vegetable colours are no longer destroyed; but though hepar acts on them like the alkalies, the mixture of which I have just spoken indicates only an acid, and the solution of heavy spar occasions an abundant precipitate. These phenomena shew that a part of the sulphur of the hepar is changed immediately into vitriolic acid by the dephlogisticated marine acid.

I added water saturated with hepatic gas to dephlogisticated marine acid; the colour and the odour of the latter were destroyed, no precipitate was formed, vegetable colours were not altered except as they are by an acid, a solution of lead was precipitated white, and the solution of heavy earth formed an abundant precipitate; but if a little dephlogisticated marine acid is added to hepaticised water it becomes clouded and a little sulphur precipitates. In the first case the dephlogisticated marine acid and the hepatic gas are destroyed on the instant and entirely, if they are employed in the correct proportions; the sulphur and the inflammable gas which holds it in solution are reduced by combination with the vital air, the first to vitriolic acid and the second to water: but in the second experiment the vital air combines at first with the inflammable gas, so that a portion of the sulphur is precipitated and can be changed into vitriolic acid only by the addition of a sufficient quantity of dephlogisticated marine acid. It is thus that a part of the sulphur is deposited in the combustion of hepatic gas.

M. DE MORVEAU says, that having mixed and agitated nitrous gas with dephlogisticated marine acid in the mercury apparatus, there was an absorption of about the fifteenth of the volume. He says also (*page 255, Dict. de Chim.*) that when this acid is in the state of liquid it does not absorb nitrous gas even when they are kept in

contact for a whole month (*ibid.*, page 263). I will in the first place remark that, as both dephlogisticated marine acid and the nitrous acid which is formed attack mercury, this apparatus is not suitable for determining the action of dephlogisticated marine acid and nitrous gas, and I have observed that nitrous gas is really decomposed and changed into nitrous acid by dephlogisticated marine acid in the liquid form ; but it is mostly in the state of gas that I have examined their reciprocal action. I mixed four measures of nitrous gas with two measures of dephlogisticated marine acid gas, a considerable redness was produced, and the mixture was reduced to 1.4 measure. By employing the calculation of M. LAVOISIER, who fixes the ratio of nitrous gas to vital air, in the composition of nitrous acid, as 69 : 40, we may conclude that the two measures of dephlogisticated marine acid contained 1.507 of vital air, which would seem to indicate that this gas has a considerable specific gravity, to contain so much vital air. However, I have not confidence in this result, because nitrous gas dissolves easily in aqua regia, as I have shewn in my Memoir on *aqua regia*, and consequently a part of the nitrous gas could have been abstracted without having really combined with vital air.

Four measures of nitrous gas, or 400 parts, were reduced to 0.35 on passing into it much dephlogisticated marine acid gas, and then absorbing the excess by water.

M. DE MORVEAU adds (*ibid.*, page 251) that dephlogisticated marine acid, after having been mixed and agitated with inflammable gas in different proportions, no longer destroyed colours, that it changed blue paper to red, that it had only a very feeble odour, and that thereafter the inflammable gas was found detonating.

Here again I have not been fortunate in obtaining the same results as this celebrated chemist on this subject ; I passed into a measured quantity of very pure inflamm-

able gas, several times in succession, an equal volume of dephlogisticated marine acid gas which did not contain atmospheric air; I agitated the mixture each time over water; the absorption of the marine acid gas having been made, the volume of the inflammable gas was not found changed. I then examined this inflammable gas with VOLTA'S eudiometer. It was not detonating; I mixed with vital air, and on detonation it destroyed quite as much as an equal quantity of the same gas which had not been agitated with dephlogisticated marine acid. As I have repeated this experiment several times, I am forced to believe that dephlogisticated marine acid has no action on inflammable gas when it is in the gaseous state, just as vital air in the elastic state has none on marine acid. I assured myself of this latter fact by a direct experiment, though it is sufficiently convincing to observe that marine acid does not at all assume the properties of dephlogisticated marine acid when it is left exposed to atmospheric air, of which about a quarter is vital air.

BERGMAN affirms that phosphorus is decomposed by the gas of dephlogisticated marine acid. M. DE MORVEAU and M. ANGULO, on the contrary, have made several experiments by which they claim to prove that phosphorus has no action on dephlogisticated marine acid. I observed, like them, that phosphorus had no action on dephlogisticated marine acid in the cold, and if heat is employed without light, the dephlogisticated marine acid is disengaged in the form of gas, without suffering decomposition; but if a morsel of phosphorus is put into dephlogisticated marine acid and exposed to light, the colour of the acid is dissipated, its odour disappears, the liquid reddens blue vegetable colours, and lime water precipitates calcareous phosphate from it; so that phosphorus combines with the vital air of dephlogisticated marine acid, and becomes phosphoric acid.

Phosphorus, which is exposed to light in dephlogisticated muriatic acid, becomes white and opaque before changing into phosphoric acid, it appears that this state is due to a portion of vital air, which is insufficient to give it the properties of an acid; it is probably thus that phosphorus whitens on the surface when it is preserved for a long time in water; when it is entirely in this state it could be compared to sulphurous acid relatively to vitriolic acid, only that it has not yet sufficient vital air to be sensibly acid. It is probably phosphorus thus combined with a portion of vital air which M. DE MORVEAU has called the *acidifiable base of phosphorus*, which he obtained by exposing phosphoric acid in a crucible to a considerable degree of heat; for the portion of vital air which was least adherent to the acid, has been forced to dissipate itself, and there was bound to remain a combination of phosphorus and a little vital air, which is less combustible and less liable to be attacked by nitrous acid, 1°, because the affinity of the phosphorus for vital air is already satisfied in part, 2°, because the heat which would be disengaged at the commencement, when the combination took place with the greatest force, cannot in this case aid that part of the combination which takes place only through a feeble affinity. It is thus that sulphur is immediately reduced to vitriolic acid if the combustion is vivid; but that, if the combustion is slow, only sulphurous acid is formed, which then assumes the state of vitriolic acid with some difficulty. It is probable that ordinary phosphoric glass similarly retains a greater or less quantity of vital air.

Chemists in general have believed that all the colours of bodies are due to one same principle diversely modified and combined in different proportions. BERGMAN in particular has attributed them to phlogiston (Mem. sur l'indigo), and he has claimed to prove by ingeni-

ous experiments that the different proportions of this principle cause the variations of colours: thus nitrous acid, which, according to him, is yellow when it has an excess of phlogiston, becomes green if water is added to it, and then blue on further diluting it. The different proportions of vital air which it is here necessary to substitute for phlogiston have a great influence on colours, as the following experiments go to prove; nevertheless nothing in general can be concluded with regard to it, for vital air gives a yellow colour to marine acid, whilst if the proportion in nitrous acid be diminished, this likewise becomes coloured yellow; for it is by driving off vital air that this acid is coloured by light, as I have assured myself by experiments which I have described elsewhere (*Journal de physique*).

The calces of iron, as may be seen in KIRWAN'S Elements of Mineralogy, and may be verified by exposing to the air a precipitate obtained from martial vitriol by fixed alkali, pass through the following gradations according as they are, as he says, more or less dephlogisticated: blue, green, brown, red, yellow, whitish. If concentrated dephlogisticated marine acid is used to dissolve iron, it gives with alkali a pale yellow precipitate; if, on the contrary, the same acid diluted with water is put on the metal it takes a blue colour, and the part which dissolves gives with alkali a blue precipitate, which soon passes to green, brown, red, and finally to a bright yellow, according as more dephlogisticated marine acid is added to it; so that the colours depend only on the quantity of vital air which unites with the iron, and it is now known that martial ethiops only differs from the other calces of iron in that it contains less vital air.

If a solution of copper is precipitated by means of volatile alkali, dephlogisticated marine acid promptly gives to the blue precipitate which has formed, a green colour



similar to that which it would take if it was left a long time exposed to air.

Not only does dephlogisticated marine acid destroy vegetable colours, so that alkali cannot restore them, but this effect equally takes place even when a quantity of alkali proper for the saturation of the disguised marine acid is put into the liquid. Among the vegetable colours that of violet syrup is destroyed instantly, likewise that of litmus; but with this latter there remains a yellow tint which resists for some time the action of the liquid; the same thing takes place with the colouring part of Pernambuco wood, and especially with that of madder. Dephlogisticated marine acid loses its properties by acting on the colouring matters, and it resumes those of marine acid, so that the colouring matters combine with the vital air and remove it from the marine acid; they thereby become soluble, but some only by means of the acid so that they can be precipitated by an alkali; others, on the contrary, are soluble in water and are not precipitated by alkali.

The green parts of plants are sometimes reduced to white by dephlogisticated marine acid, at other times to yellow; sometimes they take a reddish colour, in fact they undergo quickly changes perfectly analogous to those which air produces on them naturally; the leaves of evergreen trees resist for a long time the action of dephlogisticated marine acid, and finally take in it only the yellow tint which the air can give them.

The alterations which air produces on colours depend then principally on the vital air combining with them more or less easily, and in quantity more or less considerable; and dephlogisticated marine acid can shew in a few moments the effects which air would only produce in a long space of time: thus, whilst it destroys in a moment the greater number of vegetable colours, to destroy the

colour of indigo it requires to act during several days, and a considerable quantity of it is necessary. I shall avail myself of this means of analysis with much more detail to determine the properties of colouring matters which are employed in dyeing, and endeavour to make of the properties of dephlogisticated marine acid some applications useful to the arts.

The action of this liquid appeared to me suitable to give us information as to what happens when plants deprived of light become sickly and whiten, and to explain why plants exposed to the sun give vital air, according to the beautiful observation of M. INGENHOUSZ, and why there is no elastic fluid disengaged when they are in the shade, as M. SENEBIER has proved. The oil which enters into the composition of vegetable matters certainly contains much of the inflammable gas obtainable from water, so that it is very probable that water is decomposed in vegetation, that the vital air which it contained is in part exhaled if the light favours its disengagement, as it does for dephlogisticated marine acid and for nitrous acid, whereas without the aid of this affinity it cannot assume the elastic state; then it combines with the colouring matters if there are any formed, and the plants become white; but when the decomposition of the water is not favoured by light it takes place probably to a much less extent, vegetation languishes, the plants have much less oily and resinous matter, and thereby are even deprived of colouring matters: M. SENEBIER also observed that the sickly plants were less inflammable. This theory can be applied to a great number of the phenomena of vegetation (*Journal de phys. Août 1786*).

But dephlogisticated marine acid, which destroys all vegetable colours more or less easily, acts in a different manner on animal colours; it gives a yellow colour to silk and wool, which are white, and we know that nitrous acid

produces a similar effect. It appears then that vital air has the property of combining with animal substances, and turning them yellow by this combination.

I have not spoken in this memoir of the phenomena which volatile alkali presents with dephlogisticated marine acid, because I have detailed them in the analysis of volatile alkali; I will simply remark that when caustic volatile alkali is poured on dephlogisticated marine acid it entirely destroys the colour without producing any precipitate; and if a drop of solution of manganese is added to it a slight blackish precipitate is at once perceived.

After the explanations which I have just given I believe that it will suffice to indicate the replies that might be made to some of the difficulties which the learned chemist of Dijon believed could be solved only on the supposition of phlogiston. Manganese treated with fire gives a large quantity of vital air, it loses thereby a part of its black colour, remaining brown however; it cannot dissolve in an acid without losing part of its air, hence vitriolic acid disengages from it a large quantity of vital air on dissolving it; but, with an acid which has little action on it, it is necessary to add a substance which acts, on its part, by its affinity for vital air; such are sugar, gum, etc. If the acid which dissolves the manganese has itself affinity for the air, whilst one part unites with the manganese another part combines with the air which is disengaged from it, and it is this which takes place when marine acid is treated with this substance.

Let us pause a moment to remark that it is not by a simple affinity that marine acid removes the vital air from the calx of manganese. It is only because a portion of this acid dissolves the manganese and drives from it the portion of vital air which is superfluous to the new compound, that the other portion can unite with this vital air

deprived in part of the principle of elasticity, as the acid has only a feeble affinity for it.

The precipitate from solutions of manganese differs from manganese in colour and in properties, because it contains much less vital air, so that it cannot be used to make dephlogisticated marine acid, being deprived of that portion of vital air which could combine with the marine acid. The calx of manganese renders glass red when it is abundantly provided with vital air, this colour is dissipated when the less adherent part of the vital air combines with some carbonaceous body. The black calx loses its colour in the inner flame of the blowpipe, because fixed air is formed by the carbonaceous portion; it resumes it again in the external flame because it suffers a new calcination. Lastly, the regulus of manganese gives inflammable gas with vitriolic acid and with marine acid, because having much affinity for vital air it has the property of decomposing water; with nitrous acid it gives nitrous gas, and it detonates with nitre on account of its affinity for vital air, whereas the black calx cannot detonate because it is already saturated with this principle.

# MEMOIR

*On the development of the principles of the  
methodical Nomenclature, read at the  
Academy, 2nd May 1787.\**

By M. DE MORVEAU.

\* \* \* \* \*

Muriatic acid, from the Latin *muria, muriaticum*, had already taken the place of *marine acid* in the writings of some chemists; but it is well known that as an acid it stands apart, as it can take up an excess of oxygen and in this state its acidity appears rather to diminish than to augment, this probably being caused by the oxygen retaining a greater quantity of caloric in the compound. Whatever might be the cause of this phenomenon there is no doubt that it required a denomination appropriate to this particular character which till the present has very improperly been designated in the name *dephlogisticated marine acid*. The expressions *oxygenated muriatic acid, oxygenated muriates*, appeared to us the most simple and the most conform to the object which we had proposed to ourselves, namely, to express only well verified facts. It is by a close adherence to this rule that we have

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\*[Translated from "Methode de Nomenclature chimique, *proposé par* MM. DE MORVEAU, LAVOISIER, BERTHOLLET, and DE FOURCROY." Paris 1787. Pp. 45-7.]

formed the names of all the other compounds of muriatic acid: corrosive sublimate then becomes *corrosive mercurial muriate*; calomel, *mild mercurial muriate*; the salt produced by the ordinary dissolution of tin in this acid, *muriate of tin*; butter of tin, *sublimed muriate of tin*; Libavius' liquor, *fuming muriate of tin*, etc., etc.

Analogy leads us to believe that muriatic acid has an acidifiable base, in the same way as carbonic, sulphuric, and phosphoric acids, which equally serves to give a proper and particular character to the product of its combination with oxygen: this substance we ought not to designate otherwise than by the expression *muriatic radical* or *muriatic radical principle*; so as not to give a name to an unknown substance, and to restrict ourselves to the expression of the only property of it which we know, which is in fact to produce this acid. We have had the same circumspection with reference to all the acids of which our knowledge is no more advanced, and of which it is very possible that in the future the bases will be discovered amongst substances already named.

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# ABSTRACT

*Of the Memoirs read at the National Institute,  
from the 7th March 1808 to the 27th Feb-  
ruary 1809.\**

BY MM. GAY-LUSSAC AND THENARD.

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In our sixth memoir (Institute, 9th January 1809) we endeavour to obtain fluoric acid perfectly pure in order to isolate its radical and re-compose the acid. These researches lead us to a great number of new results, of which some are very remarkable, and give rise to our eighth memoir, which was read on the 27th February at the Institute, and has for its object the nature and comparative properties of oxy-muriatic acid gas and muriatic acid.

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*Properties of the metal of potash.*

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We have also examined the action of the metal of potash on muriatic gas. At the ordinary temperature this action is very slow; but as soon as the metal is fused there is combustion with disengagement of light, and there result muriate of potash and hydrogen gas: as the

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\* [Translated from "Mémoires de Physique et de Chimie, de la Société d'Arcueil," tome ii. Paris, 1809. Pp. 295, 298, 307 308, 320, 321, 339-358.]

quantity of hydrogen collected in this experiment is precisely the same as that which the metal would give in contact with water, and as we know, from the experiments of MM. HENRY and BERTHOLLET that muriatic acid gas contains much water, we may believe that this hydrogen comes from the action of the water of the acid on the metal, and consequently we can from this conclude nothing as to the nature of the acid.

In order to solve this question we would require to have muriatic acid free from water; but this, as will be seen by what follows, we can get only by combining it with other bodies, which then prevent its decomposition: that is why, when we treat calomel or oxymuriatic acid gas with phosphorus, we get a liquor formed of oxygen, phosphorus, and muriatic acid, of which the principal characters are that it is strongly acid, devoid of colour, and very limpid; that it becomes troubled in the course of some days; that on contact with the air it spontaneously inflames absorbent paper which has been saturated with it; that it brings about, suddenly and by itself, the combustion of the metal of potash; finally, that with red-hot iron it forms muriate and phosphide of iron, without the disengagement of any gas other than a little muriatic acid.

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*On the properties of fluoric acid, and especially its  
action on the metal of potash.*

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. . . . It is thus proved that this gas\* cannot contain water in any form, neither in the hygrometric state nor combined. Ammonia gas is absolutely in the same case,

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\* [Fluoric acid gas, *i. e.*, boron fluoride, prepared by heating fluor spar with boric anhydride.]



at least as regards combined water. But it is not the same with muriatic acid gas; it does not contain hygrometric water, it is true, but it contains it intimately combined, as MM. HENRY and BERTHOLLET first showed. We have even succeeded, by passing muriatic acid gas at a moderate heat over litharge which had been fused and then reduced to coarse powder, in extracting and collecting this water, which must form about one fourth part of its weight, according to various experiments we have made and which will be reported in the subsequent part of this memoir.

The other gases do not comport themselves with water like the preceding ones. None of them contains combined water, and all contain hygrometric water. It follows from this that fluoric acid gas,\* and probably also ammonia gas, does not contain either hygrometric or combined water, that muriatic acid gas does not contain hygrometric water and contains it combined; and that all the others contain only hygrometric water.

The most striking thing in these results is to find that muriatic acid gas contains water, and that fluoric\* and ammoniacal gases do not contain it; and especially to find that muriatic acid gas contains it in such proportions that if it were entirely decomposed by a metal all the acid would be absorbed by the oxide and transformed into metallic muriate. This is exactly what takes place, as we have assured ourselves, when muriatic acid gas is passed slowly and successively through several gun-barrels filled with iron turnings and raised to a red heat.

The more we reflect on all these phenomena the more we see that it is difficult to account for them. Might it not be possible however that oxygen and hydrogen are two of the constituent principles of muriatic acid gas, that

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\* [See note p. 33.]

they are not present in the state of water, and that this is only formed at the moment when the acid enters into combination with bodies; so that in the muriates it would be quite other than in the state of gas? Whatever may be the case this is certain, that none of the muriates undecomposable by heat, and containing only very little or no water, can be decomposed at a very high temperature either by vitreous acid phosphate of lime or by boracic acid likewise in the vitreous state; that, therefore, in the muriates the acid is held with very great force; and, that if even sulphuric acid were deprived of water, it is very probable that it could not decompose them. . . . .

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*On the nature and the properties of muriatic acid  
and of oxygenated muriatic acid.*

We had assured ourselves, while engaged on the decomposition of fluoric acid, that muriatic gas was the only one of all the gases which contained combined water, and this singular exception required us to make new researches to determine whether this water was actually essential to its intimate constitution. We first of all sought to determine the quantity of water which could be extracted from muriatic gas, and we got at this in various ways. We dissolved 27.151 grams of muriatic gas in water, cooled to  $-20^{\circ}$ , and precipitated by means of nitrate of silver. The muriate which resulted therefrom weighed 106.82 grams, representing 20.61 grams of dry acid, seeing that muriate of silver is composed of

100.00 silver  
7.60 oxygen  
25.71 acid,

consequently, the 27.151 grams of muriatic acid contained 6.54 grams of water, or 0.240 of its weight. This quantity of water contains very nearly enough oxygen to produce the oxide necessary for the saturation of the acid combined with it; for in muriate of silver, of which we have given the proportions, oxygen is to acid as 1 : 3.38; and in muriatic gas the ratio is that of 1 to 3.53.

In order to verify this result, we passed a current of muriatic gas over well-cleaned iron turnings at a dull red heat. Much hydrogen gas was disengaged, without sensible admixture of muriatic gas; much muriate of iron was at the same time obtained; the residual turnings were not oxidised, which proves that the muriatic gas contained exactly enough water to oxidise all the iron which it could dissolve. Consequently, from this result and the ratio of oxygen to silver in muriate of silver, muriatic acid must contain 0.251 of its weight of water.

Again, on decomposing oxygenated muriatic gas by ammoniacal gas, it is found to contain exactly the half of its volume of oxygen gas, and that consequently it can absorb an equal volume of hydrogen. It is further found that a mixture, in equal parts, of oxygenated muriatic gas and hydrogen gas changes, in the course of several days, into ordinary muriatic gas, and that no water is deposited. But as the specific gravity of oxygenated muriatic gas is, according to our experiments, 2.470, that of air being taken as unity, it follows that, on taking away the weight of a half part of oxygen, 0.5517, and adding to this the weight of one part of hydrogen, 0.0753, to form water, a quantity of muriatic acid represented by  $2.470 + 0.0732 = 2.5432$  contains . . . . .  
 $0.5517 + 0.0732 = 0.6249$  of water, or 0.2457 of its weight. This quantity differs little from the two preceding, so that we may conclude that ordinary muriatic gas contains 0.25 of its weight of water.

These results show that muriatic gas contains enough water to oxidise the metals which it can dissolve. It would not be possible, or at least it would be very difficult to decompose it directly. It is for that reason that, without losing the hope of decomposing it, we sought to extract it from oxygenated muriatic gas, by removing the oxygen by means of combustible bodies, as we had found that oxygenated muriatic gas does not contain combined water.

It is not possible to make use of the metals, seeing that with oxygenated muriatic acid they form neutral muriates. It seemed that the sulphides should accomplish our purpose; but, on bringing them into contact with oxygenated muriatic gas, in place of muriatic acid we obtained the sulphur liquor discovered by Mr THOMSON. The sulphites of baryta and of lime did not give us any more satisfactory results; when they were slightly moistened the oxygenated muriatic acid was certainly decomposed; but much sulphurous acid gas was disengaged. When, on the contrary, they were perfectly dry, there was no action. Neither does phosphorus separate oxygen from oxygenated muriatic gas; they combine directly, and form the liquid which we discovered by distilling phosphorus with muriate of mercury.

Finally, as a last method, we tried to decompose oxygenated muriatic gas by charcoal ignited at the extreme heat of the forge. To avoid the presence of the smallest quantity of water we made the gas pass slowly through a large glass tube a meter and a half in length, filled with muriate of lime. This tube communicated with a porcelain tube in which the charcoal was exposed to a red heat. The first portions of the oxygenated muriatic gas were completely converted into ordinary muriatic gas. This effect diminished gradually in spite of a very great elevation of temperature, and soon the gas passed without

alteration, mixed only, towards the end of the experiment, with one thirty-third of an inflammable gas, which we believe to be carbonic oxide gas. This result clearly showed us that oxygenated muriatic gas is not decomposed by charcoal, and that the muriatic gas which we had obtained at the commencement of the operation was due to the hydrogen of the charcoal, which had combined with the oxygen of the acid. In fact, on taking ordinary charcoal without igniting it, muriatic gas was disengaged during a lengthened period even at a temperature only slightly elevated, and this acid contained water, like that coming from the decomposition of muriate of soda by sulphuric acid. According as the charcoal lost its hydrogen, however, the quantity of muriatic acid went on diminishing, and finally nothing was obtained but oxygenated muriatic gas. Even plumbago changed the latter gas into ordinary muriatic gas, that is to say, muriatic acid containing water; and since the most strongly ignited charcoal produces the same change, we must conclude that it is the hydrogen gas contained in these bodies which is the true cause of the change. Oxygenated muriatic gas may thus be considered the most powerful agent that we know for depriving charcoal of its hydrogen, seeing that it demonstrates its presence even after the charcoal has been urged to the most violent heat of the forge.

After that we concluded that muriatic acid could not exist without water in the state of gas, and that oxygenated muriatic acid could not be decomposed except by bodies which contain hydrogen, or by those which, like the metals, sulphur, or phosphorus, can form triple compounds with it. New experiments confirmed us in this opinion. We found that dry oxygenated muriatic gas was not decomposed by sulphurous gas, nitrous oxide gas, carbonic oxide gas, or even by nitrous gas,

provided that they also were perfectly dry; and that it was decomposed instantly by these same gases with the help of water. Only nitrous gas when mixed with oxygenated muriatic gas slightly altered its colour, changing it to a slightly orange green; but this we doubt not should be attributed to a little water or oxygen, as we had remarked that the drier and purer these two gases were, the less marked was the change of colour.

We know, on the authority of M. BERTHOLLET, that liquid oxygenated muriatic acid is decomposed by light, and, according to M. FOURCROY, that in the state of gas it is not decomposed by this agent, or even by a very high temperature. These facts manifestly prove that the affinity of water for muriatic acid co-operates in this decomposition, and they led us to try the decomposition of oxygenated muriatic gas by means of heat along with water. We therefore arranged an apparatus enabling us to introduce oxygenated muriatic acid gas, alone or mixed with the vapour of boiling water, into a porcelain tube exposed to a red heat. In the first case the gas did not suffer any alteration; but as soon as the vapour of water was introduced oxygen gas and muriatic acid were obtained. It is not necessary for this decomposition that the temperature should be very high, as it still takes place below a red heat.

The affinity of muriatic acid for water is such as to cause the decomposition of oxygenated muriatic gas by hydrogen gas at a temperature only a little higher than that of boiling water. If a mixture of equal parts of these two gases is made and a small piece of iron heated in mercury to  $150^{\circ}$  introduced, there is a violent inflammation, and formation of muriatic acid.

Here, then, we have a body, oxygenated muriatic gas, which is decomposed neither by light nor by heat, but which, on the other hand, is decomposed quite easily by the one

or the other with the help of water. On comparing the action of these two fluids, one cannot but admit that it is identical in every case when it is exercised upon unorganised bodies. M. RUMFORD drew the same conclusion from his experiments on the decomposition of solutions of gold and of silver by charcoal, ether, and oils, by means of light and heat ; but the decomposition of oxygenated muriatic gas, which it had not been possible to effect by heat, appeared then a very powerful objection. This exception had not escaped M. BERTHOLLET in his *Statique Chimique*, and he had added to it another which he had deduced from the difference in the action of heat and of light on nitric acid ; he had, however, none the less considered their action as in general identical on almost all other bodies. Our experiments destroy these two objections, and no doubt can remain that light acts on unorganised bodies in the same manner as heat. It is enough even, in order to form a conception of the effects of the former, to admit with M. RUMFORD that it raises the temperature of the molecules on which it acts, while that of the substance in which these molecules may happen to be receives only a slight augmentation.

The decomposition of oxygenated muriatic gas by light is progressive, as it depends on the intensity of the latter. This observation suggested to us that, in a great number of cases in which compounds were formed only slowly, this arose from the fact that they were produced by an agent such as light which, in a very short time, could produce only very small effects, being in small quantity, but which, by being renewed unceasingly, produced very great effects. For it must be admitted that it would be difficult to account otherwise for the slow action which two gases mutually exercise upon one another when in uniform mixture. Since their combination does

not take place immediately they are mixed, and since it proceeds thereafter slowly, it is no longer brought about by their mutual affinity; it is due to a foreign cause which assists this affinity, such as light, heat, or electricity even.

Acting on these conjectures we made two mixtures, each consisting of about  $\frac{1}{2}$  litre of muriatic gas with the same volume of hydrogen gas, which we knew acted only slowly on one another; one of them we placed in complete darkness, and exposed the other to the light of the sun, which was that day very feeble. At the end of several days the first mixture was still coloured green, and appeared to have undergone no change; the second, on the contrary, had been completely decolourised in less than quarter of an hour, and was almost entirely decomposed. Being no longer able, after these experiments, to doubt as to the influence of light on the combination of the two gases, and judging from the rapidity with which it had operated, that if the light had been much more vivid it would have operated much more quickly, we made new mixtures, both of hydrogen gas with oxygenated muriatic gas and of the latter with olefiant gas, and placed them in complete darkness, awaiting some moments of bright light. Two days after having made the mixtures, we were able to expose them to the sun. Scarcely had they been exposed when they suddenly inflamed with a very loud detonation, and the jars were reduced to splinters, and projected to a great distance. Fortunately we had provided against such occurrences, and had taken precautions to secure ourselves against accident. Compound hydrogen gases would, without doubt, produce the same effect; but carbonic oxide gas placed in the same circumstances does not produce any alteration on oxygenated muriatic gas; a new proof that it does not contain hydrogen.



It is evident then, from these experiments, that it is light which effects the decomposition of oxygenated muriatic gas when it is mixed with hydrogen gas or with compound hydrogen gases. It is at least probable that, in all cases of slow and progressive action between bodies perfectly mixed, light has a very marked influence which doubtless extends also to the decomposition of animal and vegetable matters left to themselves. The action of light on colouring matters would doubtless be the same as that of a heat of  $150^{\circ}$  to  $200^{\circ}$ , and it would be interesting to prove that it is so.\*

Again, it is quite possible that light acts on plants only as heat, with this great difference however, that heat would raise indifferently the temperature of all the particles which compose the plant, whilst light, by acting on certain particles rather than on others, just as on liquid oxygenated muriatic acid, produces an inequality of temperature doubtless very favourable to the play of the organic forces. One thing which tends to prove this is that in plants it is only the green matter which decomposes carbonic acid. This is a new point of view, from which the chemical affinities have been, as yet, but slightly studied, and we should expect important results from it, by a comparison of the action of bodies placed in darkness with that which they exercise on exposure to light.

The experiments which we have reported up till now ought to give an idea of the constitution of oxygenated muriatic gas quite different from that which had been formed of it. It had been regarded as a most easily decomposed body, and we see, on the contrary, that it resists the action of the most energetic agents, and that

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\* Since the reading of this Memoir we have learned that light actually does act on colouring matters in this way.

it is only with the help of water or of hydrogen that muriatic acid can be extracted from it in the state of gas.

We had previously discovered that dry muriates could not be decomposed by vitreous boracic acid; but seeing from our experiments that muriatic acid could not be obtained in the gaseous state except with the help of water, we again took up these decompositions with the introduction of the action of this liquid, and carried them out very easily.

We first mixed ordinary charcoal with fused muriate of silver, and exposed them to heat in a glass tube closed at one end. Before the tube became red there were disengaged abundant vapours of muriatic gas, and the silver was found reduced. We then ignited some charcoal at the most violent forge-heat which we could produce, and put ten grams of it into a porcelain retort with twice as much fused muriate of silver. When the retort was red we obtained a little muriatic acid, and an inflammable gas burning with a blue flame; but though we increased the heat to the point of destroying the retort, only 3 grams of muriate of silver were decomposed; for all the acid collected and precipitated produced only that quantity of muriate, and we found nearly all the remainder in the retort. Strongly ignited plumbago gave us similar results. The decomposition of muriate of silver by charcoal and plumbago forced to the greatest heat having been incomplete, whilst ordinary charcoal, which retains much hydrogen, effects it completely, we must conclude that it is to the hydrogen, retained by the charcoal and plumbago even at the highest temperature, that we must attribute the muriatic gas which we obtained, and that pure carbon could not decompose muriate of silver. Muriate of mercury behaves like this latter; but its volatility does not allow of exposing it to such high temperatures with charcoal.

Finally, seeing from these results that muriatic acid was not disengaged except when the water necessary for its gaseous constitution could be formed, we put fused muriate of silver and strongly ignited charcoal into a glass tube communicating with and luted to a retort containing water. The temperature having been raised to red heat, the salt was not decomposed so long as no water vapour was passed; but the moment the water began to boil, muriatic gas was disengaged very abundantly, and the decomposition of the muriate was complete in a short time. By adding only the quantity of charcoal necessary to reduce the oxide, the silver collects very well, and we do not doubt, from the great facility with which the operation takes place, that this process can be employed on the large scale in working muriate of silver ores. This salt is decomposed by means of water, even without the assistance of charcoal, but then the oxide combines with the glass and colours it yellow. Vitreous boracic acid does not decompose either fused muriate of silver, or that of baryta, or that of soda, whilst, if vapour of water is made to pass, at a red heat, over a mixture of one of these salts and boracic acid, muriatic gas is disengaged very abundantly and borates are formed.

These experiments proving that water contributes very powerfully to the disengagement of muriatic acid, we no longer doubted that it was possible to decompose muriate of soda by water, through aiding its action by that of a body which could unite with the soda. We therefore, made a mixture of two parts of white sand with one of salt and exposed it to a red heat in a porcelain tube. In this case the salt was not decomposed, but on passing a current of steam through the tube the acid was instantly disengaged in dense and very irritating fumes, and there remained in the tube a vitreous frit of soda and silica. Alumina gives results similar to those with

silica ; when it is perfectly dry it does not decompose salt, but with the help of water it easily disengages muriatic acid. These experiments promise happy applications, as, in giving a precise idea of the constitution of muriatic gas, they indicate the means which ought to be employed to decompose muriate of soda directly.

On seeking for the bases which could be presented to the soda to separate it from salt by means of water, we had at first thought that carbonic acid would accomplish our object, as the sub-carbonate of soda is not decomposed by heat ; but we were very little satisfied with the results which we obtained. We found, in fact, that not only the sub-carbonate of soda, but also the carbonate of baryta, which cannot be decomposed by heat alone, are both decomposed with the help of water. That of lime is in the same case as the preceding ; for it loses its acid by heat more easily when the action of water is made to assist. Several of these facts were known, but there was no clear idea of the manner in which they were produced, for it was even supposed that gases could produce the same effects as steam.

We cannot, as with muriatic acid, explain the disengagement of carbonic acid by water, by saying that this liquid is necessary to its gaseous constitution ; for carbonic gas does not contain water, and it can quite well be disengaged from certain dry compounds, such as the carbonates of lime and lead, by heat alone ; it must consequently be the affinity of water for bases which favours the disengagement of the carbonic acid

This action of water for acids or for bases is thus much more powerful than has up till now been believed. This it is which determines the formation of sulphuric acid from sulphurous gas and oxygen gas or nitrous gas, and that of nitric acid from this latter gas and oxygen, as M. Humboldt has shown. It is again this action of

water which aids the decomposition of nitrate of potash by means of clay; and it is very well known in the establishments where this decomposition is carried out on the large scale, that to obtain a large yield of acid it is necessary to employ very moist clays: when they are too dry only a very little is obtained; the acid is much more concentrated, it is true, but it comes then to too high a price. The same is the case in the decomposition of muriate of soda by clay: which takes place only by means of the water which the latter contains, and stops as soon as this is all evaporated. If certain earthy muriates have been successfully decomposed by heat, this again is only because they contain water. Thus, under whatever circumstances it is sought to obtain muriatic gas, it is only possible to succeed with the help of water. Several other acids, such as sulphuric acid and nitric acid, cannot exist in their state of greatest concentration without water, which appears to be the bond which unites their elements; but water plays a much more important part in muriatic acid. In fact, oxygenated muriatic acid is not decomposed by charcoal, and it might be supposed, from this fact and those which are communicated in this Memoir, that this gas is a simple body. The phenomena which it presents can be explained well enough on this hypothesis; we shall not seek to defend it however, as it appears to us that they are still better explained by regarding oxygenated muriatic acid as a compound body.

EXTRACT FROM  
 “RECHERCHES PHYSICO-CHIMIQUES”

BY  
 MM. GAY-LUSSAC AND THENARD

(PARIS, 1811. Vol. ii., p. 262).

*Table of Facts admitted by the Authors, and contested by Davy.*

MM. GAY-LUSSAC AND  
 THENARD'S VIEWS.

\* \* \* \*

Muriatic gas contains the fourth of its weight of water or of the principles of water, and contains no more than this.

We believe that oxymuriatic gas is a compound of oxygen and another body.

We regard the liquor which is obtained by heating calomel with phosphorus as a triple compound of dry muriatic acid, oxygen, and phosphorus, and as analogous to that which is obtained with sulphur and oxymuriatic acid.

\* \* \*

DAVY'S VIEWS.

\* \* \*

DAVY is led to believe that muriatic gas contains the third of its weight of water.\*

DAVY is led to believe that it is a simple substance.

DAVY regards this liquor as a compound of oxymuriatic acid (a simple substance) and phosphorus.

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\* Since DAVY published this opinion he has announced another, according to which he regards muriatic acid as composed of oxymuriatic acid (a simple substance) and hydrogen.



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