XLI. On the oxidation of metals in general, and particularly the oxidation of iron. Read in the French National Institute

M. Thenard

To cite this article: M. Thenard (1806) XLI. On the oxidation of metals in general, and particularly the oxidation of iron. Read in the French National Institute , Philosophical Magazine Series 1, 24:95, 223-236, DOI: [10.1080/14786440608563370](https://doi.org/10.1080/14786440608563370)

To link to this article: <http://dx.doi.org/10.1080/14786440608563370>

Published online: 18 May 2009.

Submit your article to this journal [↗](#)

View related articles [↗](#)

XLI. *On the Oxidation of Metals in general, and particularly the Oxidation of Iron. Read in the French National Institute by M. THENARD*.*

As soon as oxygen was discovered, researches became general to ascertain its properties, and it was very soon discovered that this gas was the universal agent of combustion. Phlogiston was immediately exploded, and hypotheses totally contrary to experience were no longer resorted to in order to explain the generality of phenomena. By admitting the presence of this principle, more or less, in the metallic calces, an exact account may be taken of the augmentation of weight which metals receive when calcined. But, however simple this theory may appear at present, it was nevertheless the result of a grand effort of genius.

When it was clearly demonstrated that metals, as well as other bodies, so far from losing their principles by combustion, absorbed a new one, because they are thereby augmented in weight; when Lavoisier taught us, that in this phenomenon, the cause of which was for such a long time unknown, the atmosphere was decomposed, and that one of its constituents formed a new combination, the properties of burnt bodies were examined with more care; a great number of new principles were discovered in such bodies, and in many of them the quantities of oxygen and of the radicals which formed them were determined. These new observations were again the source of many discoveries. It was seen that the same combustible body might be combined with oxygen in different quantities, and that consequently several oxides, as well as several acids, might have the same radical. Frequent applications of this principle are met with, particularly in the oxidation of metals; and at this period, lead, antimony, and manganese, offer the most remarkable of these applications. It was this variety of oxides which led the author of the Chemical Statics to think that there actually was not so much difference as had been previously believed between oxides of the same genus; and

* From *Annales de Chimie*, tome lvi.

this led him to believe, supported also by reflections which were the result of many experiments, that probably even metals pass from the metallic state to the maximum of oxygenation by going through all the intermediate degrees of oxidation in such a manner, that for each metal there is a multitude of different oxides.

I am well persuaded that the number of metallic oxides is much greater than most chemists admit, and that they do not pass immediately, as is supposed, at least with respect to some of them, from a weak degree of oxygenation to a very high one; that between these last there exists one or more intermediate degrees which constitute as many particular oxides: but I confess that I am not yet convinced that there are as many oxides as possible degrees of oxygenation; and if the theory admits them, experience seems to reject them: in fact, why should not these different oxides combine with acids? The cause cannot be attributed to any thing else than that metals, at a certain degree of oxidation, have more affinity for acids than at any other; but for that very reason it may happen, that, when combined with a given quantity of oxygen, they may form fixed oxides, while with a greater or less quantity these oxides can only have a momentary existence. The latter would therefore be placed between the former; there would be as many degrees through which the former would be obliged to pass without being able to stop; and besides, this is exactly what we observe of acids which have the same radical. Will it be said, that between the *sulphurous* acid and *sulphuric* acid, between the *phosphorous* and *phosphoric* acids, there are several intermediate acids? And if these intermediate acids do not exist; if sulphur, phosphorus, &c. cannot form any more than two acids, why do metals give birth to such a multitude of oxides? why should not there be fixed degrees of oxygenation as well for the one as the other? In short, how could it happen that hydrogen forms only one oxide, although susceptible of fixing more than five times and a half its weight of oxygen? There are many reasons which incline us to believe that metals are absolutely like other combustible bodies; and although it is proved that the latter cannot form, with the general

neral principle of combustion, a multitude of different combinations, I am persuaded that metals, which we regard with reason as analogous bodies, are not more susceptible than the others of a multitude of different degrees of oxidation.

If we are permitted to entertain doubts on this view of the subject, we may certainly have some upon the nature of the oxides in their combinations with acids; and even if this truth had not been long admitted by chemists, some general observations would suffice to place the subject in a clear point of view. Let us take a glance, however, of each of these oxides, and attentively consider the oxides of iron, which are the principal objects of this memoir. Here every thing demonstrates, that in combinations of this sort the oxides are constant. Although cobalt, nickel, lead, zinc, gold, and platina, are all the bases of several oxides, yet in all the salts which they form they are always equally oxidated: thus the oxide is blue in all the salts of cobalt, green in those of nickel; it is white in those of bismuth, zinc, and lead; and it is gray in those of silver, yellow in those of gold, and brown in those of platina: it varies, to be sure, in the salts of antimony, tin, mercury, copper, and iron; but still with several of them it is only certain of their oxides that can unite with acids. Two white oxides of antimony alone are susceptible of this combination—the white volatile oxide and the white oxide of the second degree; the white oxide at the maximum is not attackable, except by the muriatic acid: still, however, if it is not in a state of very minute division, the muriatic acid dissolves it with great difficulty, and always by partly passing to the state of oxygenated muriatic acid. Tin, mercury, and copper, like antimony, do not form saline combinations with the acids, but under two states of oxidation; tin in the state of a gray and a white oxide, mercury in the state of a black and a red oxide, and copper in the state of a yellowish white and a brown oxide.

Hitherto it was thought that it was the same case with iron, and that in all the salts which it was susceptible of forming, the oxide was always green or red. Some chemists, however, have admitted an intermediate oxide: they believed

Vol. 24. No. 95. *April 1806.* P that

that there was also a yellow oxide, because ferruginous salts present themselves sometimes under this colour. Reasoning upon the hypothesis that all the metallic salts were always of the same shade as their oxides, they were necessarily led to adopt that idea; but it is now very well known that this method of viewing the subject is often erroneous, and that a salt is often white or red although its oxide is red or blue. Another salt, consequently, might be yellow, and have a red oxide for its base: this is exactly the case with all the yellow salts of iron. Besides the green and red oxide, however, there exists another oxide of iron which performs a very important part in the ferruginous saline combinations; and as, on the one hand, the formation of several productions manufactured in the workshops, and, on the other hand, as the explanation of several phænomena, which often present themselves in the arts, depend upon the existence of this oxide, I think it my duty to enter into some details respecting it.

It is formed when iron is treated with most of the acids; and we obtain it by decomposing by means of potash, soda, and ammonia, the various salts so formed. Above all, by means of a solution of iron in sulphuric acid we may easily demonstrate its existence. If in this recent solution we pour some alkali, a white precipitate is formed, which becomes speedily green at the surface and soon passes to a red colour*. These changes of colour, which take place in the whole mass if it is agitated, are evidently produced by an absorption of oxygen; because, in repeating the experiment in a flask, the air which it contains sensibly diminishes in volume, and soon extinguishes a taper plunged into it, when the white oxide has become green, and with greater reason when it has passed to the red.

It is this white oxide, hypersaturated with sulphuric acid, which forms, in a great measure, the sulphate of iron used

* I poured some hyperoxidated sulphate of iron into a great excess of caustic potash, and I always observed a white precipitate. I even boiled the mixture in a retort the neck of which was plunged into water; the oxide became green, and was even red at the surface; but the lower part was always perceptibly white, although it contained no sulphuric acid. Of this I convinced myself by washing it, dissolving it in the muriatic acid, and by adding nitrate of barytes to it.

in commerce. Nevertheless, besides this combination, the white oxide may still form a sulphate much more acid; and then, instead of being of a dark green, the compound approaches to a clear emerald green. Thus we find there is a green oxide as well as a red oxide of iron; each of them, on being united with sulphuric acid, gives birth to at least two very distinct salts. Let us now proceed to examine these six kinds of sulphate of iron.

I shall distinguish the first of them by the names of acidulated sulphate and acid sulphate of white iron, because the oxide in these is colourless, and the one much more acid than the other; the second, for the same reason, under the names of acidulated sulphate and acid sulphate of green iron; and the third, for the same reason, I shall term neutral and acid sulphates of red iron.

The acidulated sulphate of white iron is obtained by boiling sulphuric acid diluted with water upon an excess of iron filings or turnings. When dissolved, or in particular crystallized, it is always of a bottle green, and the more coloured it is, the more is it esteemed in commerce. It instantly loses this colour upon an addition of sulphuric acid; it then takes an emerald green and becomes acid sulphate of white iron, which alters blue colours much more than the former*: it is then less fit for the operations of the arts, and rejected by manufacturers, who give a preference to the former, not from prejudice, but founded on the nature of saline

* When sulphuric acid is poured into a solution of acidulated sulphate of white iron, evaporated in such a manner as to mark 36° to the weight of the liquor, it almost immediately forms an abundant white and crystalline precipitate, which is nothing else but acid sulphate of white iron. This is the reason why, in vitriol manufactories, it sometimes happens that the liquor becomes all at once troubled to a certain degree, and leaves a deposit of a white matter, which is rejected by the manufacturer, and gets the name of magnesia. The solution is then too acid, and the escape of this excess of acid takes place instantly, so as to form an acid sulphate which is precipitated, and an acidulated sulphate which remains in solution and crystallizes much more regularly than the first. This inconvenience might be guarded against by boiling the solution a longer time with iron, and adding water to it, if necessary; because the acidulated sulphate of white iron or the sulphate of iron of commerce, when it is too much evaporated, is also susceptible of partly concreting itself; at least it sometimes does so suddenly, all in a mass.

compositions; it may be transformed also into acidulated sulphate by heating it with iron; this is what is done in several vitriol manufactories, and particularly at Beauvais, where this salt is extracted from pyritous turf, which is burned, and which without that would yield acid sulphate, less beneficial in commerce. This may be done with every kind of acid sulphate, whatever is its origin; whether natural or artificial, the transformation always takes place: it would still be made whether the oxide of iron was green or red. The acidulated and acid sulphates of white iron are both precipitated white by the alkalies; they instantly decompose oxygenated muriatic acid, and pass, in proportion as more or less of it is introduced into them, to that state of sulphate in which the oxide is green or red; it is in this manner that the oxygenated muriatic acid acts upon the pure white oxide; such also is the action of the air upon the combinations of this oxide with acids, and particularly with sulphuric acid. This is the reason why the colour of these solutions is not constant; from the green they pass to the red; the liquor is troubled, deposits a yellow matter, and then ceases to be coloured. All these phenomena may be explained from natural causes, and are the consequences of the properties which the other sulphates of iron present to us, of which we are now about to speak.

The acidulated and acid sulphates of green iron, both of which result from the combination of the green oxide of iron with sulphuric acid, present the most striking differences. The first (being that which is only a little acid) does not crystallize at all, not being able to exist except in a liquid state; if submitted to evaporation it absorbs oxygen from the air, becomes troubled; and deposits neutral sulphate, yellow, insoluble, and very much oxidated: thus it transforms itself into acid sulphate, in which the oxide is always green, but itself almost colourless, and which resists every kind of decomposition much more than the other: although it has green oxide for its base, it is red itself: this is what occasions the error of most chemists, who, down to the present moment, have regarded it as a sulphate very much oxygenated: thence it again happens that the acidulated

lated sulphate of white iron, the solution of which is of a fine green, reddens on its exposure to the air.

Oxygenated muriatic acid converts it all at once into acid sulphate highly oxidated; iron, on the contrary, converts it into acidulated green or little oxidated sulphate, the sulphuric acid makes it lose its red colour immediately, by transforming it into an acid sulphate almost colourless, or at least only slightly green. This acid sulphate may be crystallized by a well managed evaporation; the crystals formed are something of an emerald green colour, and in this respect it approaches an acid sulphate little oxidated; they do not sparkle nor deliquesce; their solution in water, which is but little coloured, does not, like the acid sulphate of white iron, absorb oxygen till after a long time: the excess of acid which they contain fixes to a certain degree the oxide of iron; nevertheless by means of oxygenated muriatic acid the oxide becomes red; and by means of iron it passes to the state of white oxide, particularly at the temperature of boiling water. Both the acidulated and acid sulphates of green iron precipitate themselves green by means of the alkalis. The precipitate contains no acid when a great excess of base is added, and particularly when heated: in every instance it is green. It is by treating the red oxide of iron with diluted sulphuric acid that we obtain the acid sulphate of red iron; the solution would not take place if the acid were concentrated. The acid sulphate of red iron contains more acid in excess than the acid sulphate of green iron, and the latter much more than the acid sulphate little oxidated. These properties are common to them with all oxides of the same kind; they require the less of any acid for their saturation the less oxygen they contain; and, on the contrary, they require the more acid the more they are oxygenated; this is proved by antimony, mercury, tin, copper, and iron. They alone among all the metals combine with acids at different degrees of oxygenation; and all, without exception, are subject to this law. This is the reason why the solution of muriate of tin little oxidated becomes troubled by the contact of the air, or when being crystallized we attempt to dissolve it. It is also for this reason that this

same recent solution of tin entirely decomposes corrosive sublimate and revives the mercury, not only taking the oxygen from it, but even the muriatic acid. Thence it also happens that the acid sulphate of white iron transforms itself in part, by absorbing oxygen from the atmosphere, into green acidulated sulphate, and assumes a slight red tint; thence it happens at last, that this same salt, when it is only acidulated, becomes troubled all at once upon pouring aerated water into its solution: several other phenomena depend upon the same cause; but, should I insist longer on this branch, I should wander too far from the subject on which I propose to treat.

Like the two other acid sulphates, the red acid sulphate of iron is almost colourless; it takes a very strong colour, and reddens when its excess of acid is saturated in part by potash; by adding a greater quantity of a salifiable base, a neutral sulphate is precipitated from it, which is, however, susceptible of being decomposed by the alkalis: it separates, as well as all the highly oxygenated salts of iron, sulphur from hydrogen, and returns to the state of a very acid green or white sulphate of iron; it yields no crystals upon evaporation: the iron changes it into a less oxygenated sulphate.

I have but little to say of the highly oxidated neutral sulphate: it is yellow and insoluble; this is the sulphate which in time, by exposure to the air, is precipitated from solutions of green or white acidulated sulphate: this is also the sulphate which is deposited when the solution of green acidulated sulphate of iron is evaporated, and which from being red becomes almost colourless, because then it passes to the state of acid sulphate; it is this salt, in short, which chemists formerly took for a particular oxide, and which induced them to admit a yellow oxide of iron, as intermediate between the red and the green.

The action of the muriatic and nitric acids upon iron resembles much that of the sulphuric acid; that of the muriatic acid does not differ at all, but the acid muriates of iron are not so well characterized as the acid sulphates; the muriate when little oxidated crystallizes very well, and the crystals formed from it are of a fine green; but when the solution

tion is exposed to the air, the iron becomes more oxidated, and as it then requires a greater quantity of muriatic acid to dissolve it, it is partly precipitated. No nitrate, however, exists in which the oxide is white. We can only obtain green and red nitrates of iron; the first is formed by taking five parts of the acid, and the second by employing twelve or fifteen parts of acid. If the acid was more concentrated, a portion of the red oxide would be precipitated, and very little of it would be found in solution, if it contained from thirty-six to forty parts. This precipitation would not take place, unless the red oxide was very little divided: it is to this cause that we ought to attribute the inaction of the nitric acid upon colcothar, as well as the little action which sulphuric acid itself has upon this substance. What proves this is the property which these two acids have of easily dissolving the red oxide in the gelatinous state, or recently precipitated from the nitrate or muriate by alkalis.

We find in the other acids the same mode of action as in the sulphuric acid; but the generality of salts which result from them, being insoluble, are rather obtained by means of double decompositions than directly. I shall not here take notice of all the saline bodies, on account of the little interest they have hitherto excited in the arts and sciences; I shall only examine the two most important,—the gallates, which serve as the bases of the black dye; and the prussiates, the use of which has so much increased for these thirty years past.

We know that the gallic acid attacks iron even at the temperature of the atmosphere; that it dissolves it with the disengagement of that proportion of hydrogen gas necessary when water is decomposed; that this solution, at that time colourless, becomes blue very soon on its exposure to the air; and that then it begins to be thick, and passes to a blackish gray. All these phænomena have been described with much care by M. Proust, but to this moment the whole have not received a satisfactory explanation. I discovered the cause of their difference in the three oxides which iron is susceptible of forming. Thus, by pouring gallic acid into acidulated sulphate of white iron, no precipitate is obtained;

with the acidulated and acid sulphate of green iron it forms a precipitate of a fine blue; and by repeating the experiment with a highly oxygenated salt of iron, the matter deposited is of a black inclining to gray. An excess of acid, however, hinders the deposition from taking place. This is what we remark in the acidulated sulphate of white iron, where the addition of an alkali is indispensable for the formation of the gallate which then presents itself under the form of violet-coloured flakes; this is also what is observed in red acid sulphate of iron, where the saturation of the acid is necessary for the precipitation of the composition; this, on the contrary, does not take place in the red muriate of iron which is only a little acid.

The three oxides of iron of which we have been speaking, and all of which may be combined with acids, form combinations with the prussic acid much more multiplied than those we are about to examine. Not only do prussiates of iron exist, neutral and with an excess of oxide, but both the one and the other are susceptible of uniting with the prussiate of potash and forming triple insoluble salts, if the metallic prussiate predominates; and, on the contrary, it will form soluble salts when there is almost nothing in it but alkaline prussiate. Such, in few words, is the general history of Prussian blue; but it is of too much importance to science not to consider particularly every one of its component parts.

One department of this history, the most useful to study, is the difference of colour in the precipitates obtained by decomposing solutions of iron by the alkaline prussiates: the shades of these precipitates are singularly various. Sometimes they are white, and sometimes greenish; but oftenest they are more or less blue, and the eye accustomed to judge of colours recognises many different shades in these principal colours. These effects do not depend entirely upon the state of the oxidation of the iron; they depend also upon the state of the alkaline prussiate and the metallic solution.

If the iron is little oxidated, the solution but little acid, and the prussiate has an excess of alkali, a white precipitate will be obtained; it will be greenish white, if, while the
other

other circumstances are the same, the prussiate is neutral; the one differs from the other only in the proportion of their constituent principles; the former contains an excess of oxide, while in the latter the acid is merely saturated with it. Thus the acids instantly render the prussiate of white iron greenish, by taking from it a part of its base; and the alkalis make the slightly green prussiate of iron pass to a white colour, by attracting to themselves a part of the acid which enters into its composition: thus by art we may transform these two salts, the one into the other at pleasure, merely by varying the quantity of the substances which form them.

These precipitates are not simple prussiates of iron, as has been believed for a long time; they contain besides prussiate of potash, as Berthollet has proved. The prussiate of potash has even so much affinity for the prussiate of iron, that the sulphuric acid only decomposes in part the insoluble combination which these two salts form together. If a slight excess of acid only is added, the residue still contains plenty of potash, and is perceptibly green; it becomes greenish blue by a greater quantity of acid, and, when analysed, little alkali and oxide is found in it: this attraction is still more striking when the prussiate of potash is abundant enough to render the combination soluble; then the sulphuric acid does not disengage from it even the most trifling smell of bitter almonds, and the sulphate of iron uniformly produces a very great quantity of precipitate; while, if the alkaline salt is pure, the carbonic acid is powerful enough to disengage the prussic acid from it.

The same results are obtained by substituting, in place of the acidulated sulphate of iron not much oxidated, the green acidulated sulphate of iron and the red muriate of iron which is only little acid: its precipitates are always triple prussiates of iron and potash; that one the oxide of which is green, is less blue than the one the oxide of which is red; both change colour if united with a great excess of oxide; the first becomes yellowish white, and the second reddish yellow; if the excess of oxide is less, they approach nearer to a blue colour; but both the one and the other are susceptible of being brightened by the acids.

Six prussiates of iron therefore exist, which are well characterized ; three of them are neutral, and three with an excess of oxide ; the excess of oxide may be more or less considerable, which varies in a singular manner the colour of these prussiates. These six prussiates of iron may be combined with different quantities of prussiate of potash, and without doubt also with the other alkaline prussiates, in such a manner that this genus of salts is very numerous in species. It is generally observed that those which contain much alkaline prussiate are soluble ; those, on the contrary, which contain much prussiate of iron are insoluble. We know that Prussian blue becomes green by exposure to the air, and that it then forms red oxygenated prussiate of iron. When the ordinary prussiate of potash is boiled with Prussian blue, which is thus oxygenated in whole or in part, the oxygenated prussic acid acts upon the potash, and the prussic acid combined with it acts upon the oxide of iron in such a manner, that the filtered liquor precipitates the red nitrate or muriate of iron of a green colour. This is the reason why certain solutions of prussiates, made by means of Prussian blue, precipitate the sulphate of iron little oxidated in a white colour instead of a blue one.

It is this variety presented by prussiates in their composition, which renders their preparation so difficult. This, however, is not the only obstacle we meet with in the manufacture of Prussian blue ; there are still a great many others, which were only surmounted after a long time, and some of them even exist at this moment. One of the perfections necessary to be attempted in this art, would be to save for other uses the great quantity of carbonate of ammonia formed by calcination, which would admit of the prussiate of iron being used with much more advantage in commerce. I am convinced, by experiments made with great care, that on calcining potash with animal matters, as much carbonate of ammonia and prussiate of potash is obtained as when such animal matters are distilled by themselves ; so that as much prussiate of iron is formed with the carbon resulting from their distillation, as with all their principles united. We may thus make sal-ammoniac at the
same

same time with Prussian blue, and consequently double the products without much augmenting the expense of the manufacturer. The manufacturers of Prussian blue ought not only to direct their attention to this point, but also to several others which might improve their different processes. Some do not employ the most advantageous proportions of potash and blood, some do not add iron, and several maintain the heat too long: only a very few of them take the trouble of crystallizing the prussiate of potash; many of them do not know that in the calcination of substances the sulphate of potash contained in the potash made use of is transformed into sulphurets, and for a much stronger reason they are ignorant of the means of preventing the bad effects of it. In short, almost the whole of them consecrate too much time in oxygenating Prussian blue; by that means augment the manual labour, and deprive themselves of the power of making more considerable quantities of it. The prosperity of their manufactories depends, however, on all these considerations united.

The following is what I have remarked on this point :

Experience has proved to me, that a quantity of potash equal to that of blood was preferable to every other proportion; we know that the addition of iron favours the formation of prussiate of potash, and fixes it. It is not less evident that the effect of fire is also as important to observe, because, by exceeding the point of fusion, we decompose the prussiate of potash, or the matter which ought to form it. It is equally necessary to crystallize the prussiate of potash, particularly when we wish to obtain Prussian blue of a superior quality. On the one hand, we thus transform the sulphurated hydro-sulphuret of potash into sulphate of potash; and, on the other hand, it is only necessary to add very little alum in order to saturate the excess of alkali: we might again decompose the sulphurated hydro-sulphuret of potash by means of the sulphuric acid, because the acid does not alter the prussiate of potash combined with a certain quantity of prussiate of iron. This crystallization is not indispensable in the fabrication of common Prussian blue, into which much alumine enters, which cannot be separated
but

but by a great quantity of potash ; it is sufficient to boil the liquor some time in order to burn the hydro-sulphuret ; and, besides, the sulphurated hydrogen is separated by the acid of the alum. In short, the operation would be very much abridged, if, instead of washing the prussiate of iron in a great quantity of water, it was only mixed with a small quantity of oxygenated muriate of lime.

Such are the observations which I considered it my duty to collect in the present memoir ; the whole facts do not belong to my subject. In order to support those which do, I have connected with them some observations which were the result of the labours of different chemists. Sometimes I have even repeated facts known long ago, in order to present at one view the properties of a body, or the track we ought to follow in an operation. Yet still, I believe, I have examined, with some advantage to the arts and sciences, the oxidation of iron and the combinations of its oxides with acids. The existence of the white oxide of iron will make us acquainted with various phenomena the causes of which were hitherto unknown ; it explains, in particular, that variety of colours which all the ferruginous salts present to us. It spreads some light on one of the finest and most important dyes known, viz. that of black. It does not throw less light on the manufacture of Prussian blue, upon the improvement of which much yet remains to be done. In short, it deeply concerns the art of obtaining sulphate of iron, the perfection of which becomes daily more and more desirable.

XLII. *On the Combination of Antimony with Tin.* By
M. THENARD*.

I WAS led, about a year ago, to make the observations I am now about to communicate, upon examining an alloy attempted to be introduced into commerce, and to which such miraculous properties were improperly attributed, that, according to some accounts, it might have been substituted in place of silver.

* From *Annales de Chimie*, tome lv.