XL. *On the Composition of an Acid Oxide of Iron (Ferric Acid).* By J. DENHAM SMITH, Esq.

Read May 16, 1843.

IN the autumn of the year before last, whilst pursuing some investigations respecting the alleged conversion of carbon into silicon, I remarked that when the residuum of the calcination in close vessels of ferrocyanide of potassium (carburet of iron) was fused with carbonate and nitrate of potash, and the resulting compound treated with water, a solution of a deep amethystine red colour was produced; this rapidly decomposed, evolving oxygen gas, and depositing sesquioxide of iron, until the decomposition being completely effected, it became quite colourless; no manganese could be detected in the solution, nor in the deposit, although the colour of the former was precisely similar to the permanganate of potash in solution.

Remembering that the combination of an oxide of iron with potash was already on record, but unable to recall to memory the publication in which it was noticed, I am indebted to the Editors of the *Philosophical Magazine* for referring me to the *Journal de Pharmacie*, tom. xxvii. p. 97, where I found a communication from M. C. le Fremy, upon "The Action of the Alkaline Peroxides on Metallic Oxides." Since the appearance of this memoir, which has been followed by researches by the same author on the combination of potash with the oxides of zinc, tin, &c., various notices have been published by MM. Trommsdorff, Wackenroder and Poggendorff, on the subject of this combination of oxygen, potassium and iron, confirming the existence of this purple-red compound, and pointing out various modes of obtaining it.

I had expected that M. Fremy would have extended his inquiries and ascertained the composition of this new oxide of iron; but as a considerable period has elapsed since his original notice of its existence, and his subsequent researches in connexion with this subject having taken other directions, other chemists also having investigated the compound, and as my own experiments were commenced before I was referred to M. Fremy's paper, I may be excused for having thus directed my attention to the composition of a substance, to the priority of the discovery of which I have no claim, although I had ascertained its existence independently of the observations

of the French chemist. I have entered on this explanation, as I would in nowise wish to deprive M. Fremy of his just claim to the original notice of this compound; but as my previous observations and pursuit of the subject were entirely independent of M. Fremy's notice of its existence, I feel myself justified in communicating the results of my investigations, especially as its first discoverer appears to have abandoned the pursuit.

In the memoir in the *Journ. de Pharm.* already alluded to, various modes are pointed out for preparing this combination of potash and oxide of iron, which is obtained by igniting a mixture of sesquioxide of iron, potash and nitre, or peroxide of potassium and sesquioxide of iron, or by calcining at a full red heat potash and sesquioxide of iron; by these means a brown substance was procured which afforded a deep violet-red coloured solution, very soluble in water, but which solution is easily decomposed; concentrated solutions of the alkalies precipitate it of a brown colour, which precipitate redissolves on the addition of water; it decomposes rapidly by an elevation of temperature, and instantaneously by the contact of organic substances. The same coloured solution may be formed by passing a current of chlorine through a concentrated solution of potash, holding precipitated sesquioxide of iron in suspension. The German chemists prefer deflagrating dry nitrate of potash with half its weight of iron-filings at a temperature approaching to visible redness, and also direct the employment of chlorine gas, potash and precipitated oxide of iron, as mentioned by M. Fremy, to procure it. M. Pogendorff found that when a current from Grove's battery is passed through a solution of one part of hydrate of potash in four of water, using *cast iron* for the positive pole plunged in the potash, and wrought iron or any other convenient metal as the negative pole, ferrate of potash was formed in the solution, which immediately becomes dark red and opaque. Wrought iron and steel do not produce this compound, but evolve oxygen gas; the red solution soon decomposes either with or without the continuance of the passage of the electrical current, oxygen gas being liberated and sesquioxide of iron precipitated.

To prepare this compound I have found the subjoined process attended with very uniform success:—Wash the ferri sesquioxide of the shops with boiling water until free from sulphate of soda, dry and ignite at a low red heat; this furnishes a very pure oxide of iron and in a state of minute division; one part of this is to be intimately mixed with four of dried nitre, reduced to fine powder; place this mixture

in a crucible of about twice the capacity of the bulk of the mixture, lute a well-fitting cover on, making a few small holes in the lute to allow the escape of gas, and ignite at a *full red* heat for about an hour, if six or eight ounces are made: the time of ignition depends much on the quantity prepared, and the temperature should never be raised above a full red. When well prepared it presents the appearance of a dark reddish-brown porous mass, rapidly deliquescent on exposure to the air, so that I have found it advantageous to powder it whilst still warm, when it may be preserved for use in a well-stoppered bottle, apparently for any length of time.

To examine the solution of this substance it is most convenient to employ ice-cold water, as much heat is evolved when it is thrown into water, and the decomposition of the solution is augmented or retarded by the elevation or depression of temperature. On the addition of water it evolves much oxygen gas with effervescence, probably owing to the decomposition of peroxide of potassium; if the water employed be ice-cold and the vessel containing it plunged in ice, the decomposition of the solution will be retarded. By allowing the mixture to subside for a few minutes, a solution is obtained almost free from oxide of iron in suspension, of so deep an amethystine red colour as to be apparently opaque except at the edges, but by dilution its colour is readily perceived; it gradually decomposes, evolving oxygen gas and depositing sesquioxide of iron; heat facilitates this decomposition; at 212° F. it is completely effected, and the solution remains colourless. It is decomposed, evolving oxygen, by sulphuric and nitric acids, chlorine is liberated by the addition of hydrochloric acid; by oxalic acid, carbonic acid gas mixed with oxygen is given off. It affords no precipitate with the salts of lime, magnesia, or strontian, but on the addition of a barytic salt a voluminous crimson-red precipitate falls, which may be washed, collected and dried at 212° without changing colour. With the metallic salts, the bases of which are capable of combining with more than one equivalent of oxygen, as nickel, manganese, &c., it produces the superoxide of these metals, but with the salts of zinc and metals combining with but one equivalent of oxygen, it precipitates their oxides and evolves oxygen gas.

When the deep pink-coloured solution is prepared by passing a current of chlorine gas through concentrated solution of potash holding oxide of iron in suspension, or through the deep amethystine solution already described, keeping the vessel cool during the passage of the gas, the solution obtained

is of a lighter colour than the amethystine liquid and very permanent, it having been kept for months in close vessels without decomposition being completely effected, the gradual progress of which however is shown by the deposition of a light brown substance (sesquioxide of iron?). This chlorinated solution may even be evaporated and a pink salt obtained, but I have been unable to isolate by any means I have attempted the potash salt of this oxide of iron. I may add, that the characters assigned to these two solutions by the French and German chemists are generally in accordance with my own observations.

Although foiled in my endeavours to obtain the potash salt free from admixture of other salts, I was yet enabled to deduce from it the composition of this new oxide of iron, which in accordance with my suggestion, Sept. 1841, is now usually called ferric acid, and subsequently to confirm this constitution by the analysis of the barytic salt.

The mode of analysis was extremely simple, being founded on the perfect decomposition of the deep amethystine solution at 212° . A solution of the reddish-brown fused mass was prepared with ice-cold water and with the precautions before described; when the insoluble portion had subsided, which it did rapidly, and a portion of the solution had been tested by withdrawing it by a tube and mixing with a large quantity of distilled or of lime water (which latter seems to possess the property of checking the rapidity of the decomposition of this potash salt when very dilute), to ascertain whether the subsidence of the uncombined oxide of iron was so complete that an apparently inappreciable quantity was held in suspension; a certain quantity of this clear amethystine solution was transferred to a retort of a known capacity—leaving, of course, a portion of atmospheric air in the upper part of the body and in the neck of the retort; this quantity of air was accurately determined by previous measurements and graduation of the retort; heat was then applied, and the contents of the retort raised to violent ebullition which was continued so long as any gas was evolved; these gaseous products were collected over water, and when no more gas was liberated absorption was allowed to take place by withdrawing the lamp from the retort; any air which the retort then contained was added to that already collected, and when the gas had acquired the temperature of the surrounding atmosphere, it was measured, the known bulk of atmospheric air originally contained in the neck and upper part of the retort subtracted from it, and the residue, oxygen, corrected for temperature and pressure.

The oxide of iron deposited during the boiling was dissolved in hydrochloric acid and estimated in the usual way.

I subjoin the detail of an analysis as an example*. The results of several successive experiments are contained in the following table: —

Exp.	Cub. in. at 60° and 30.	Grs. of oxygen.	Grs. ox. iron.	Total wt of oxygen.	Weight of iron.
1	12.3	4.2	16.4	9.12	11.48
2	9.38	3.37	12.6	7.15	8.82
3	13.03	4.45	16.8	9.49	11.76
4	5.21	1.78	7.2	3.94	5.04
5	14.70	5.03	22.3	11.72	15.61
6	7.58	2.59	10.6	5.77	7.42
7	33.41	11.41	42.0	21.01	29.40
	96.11	32.83	127.9	71.20	89.53

The mean of these experiments gives 22.27 parts of oxygen by weights to 28 parts or one equivalent of iron, which is equal to a deficiency of 1.74 parts in three equivalents, or 24 parts of oxygen. This is, I submit, an approximation sufficiently near to three equivalents of oxygen to one of iron, to justify me in adopting the formula FeO^3 , as representing the constitution of this acid oxide of iron; especially when we consider that the circumstances under which the experiments were made would indicate the probability of some free sesquioxide of iron being suspended in the solution, as, from the unstable nature of the compound, a short period of time only could be allowed for the deposition of any insoluble matter, and the impossibility of subjecting it to filtration, owing to its decomposition by the contact of organic substances. This excess of oxide of iron varies in the different experiments quoted, so that whilst Nos. 4, 5, and 6 afford 21 to 22 parts oxygen to an equivalent of iron, 1, 2, 3, and 7 all exceed 22 of the gas to an equivalent of the metal, the last, No. 7, especially; and this experiment being the one upon which I am inclined to place the greatest reliance from the concentrated and clear state of the solution, gives nearly 23 parts (22.85) of oxygen to 28 iron. This cause, together with a certain amount of decomposition during the transference from the vessel in which the solution was made to the retort, affords an explanation of the deficiency in the quantity of oxygen as indicated in every experiment, in comparison with that which I theoretically assign to this compound.

* A retort filled to a certain limit with the solution left 13.75 cub. in. of atmospheric air in the body and neck of the retort, and gave 26 cub. in. of gas at a temperature of 58° , and barometer at 29.926 — 13.75 air = 12.25 oxygen corrected, weighs 4.2 grs. The oxide of iron freed from silica by hydrochloric acid and ammonia, gave 16.4 grs. of sesquioxide = 11.48 iron, and 4.92 oxygen + 4.2 = 9.12 oxygen combined with 11.48 iron.

In no one case was the quantity of oxygen actually obtained so small as to indicate a compound of 20 parts of oxygen to 28 of iron ($2 \text{ Fe} + 5 \text{ O}$ or $\text{Fe}^2 + \text{O}^2$), and I do not consider the formula intermediate with this last and the constitution I have assigned to the oxide, is a very probable one to exist, being $3 \text{ Fe} + 8 \text{ O}$; moreover, in four out of seven experiments more oxygen was obtained than such a compound could evolve.

The conclusion at which I arrived, that this ferric acid is a *teroxide of iron*, is confirmed by the subsequent examination of the insoluble crimson compound it forms with barytes. This salt is readily formed by adding an excess of a dilute solution of a barytic salt to the clear amethystine solution, which, prepared as I have described and dissolved in close vessels, will not contain the sulphates in any marked quantity, nor any carbonic acid whatever, the precipitate being washed in vessels excluded from the atmosphere with freshly boiled distilled water, to prevent the access of carbonic acid to the alkaline solution, and drying at 212° F . It is of a dark crimson red colour, decomposable before drying by the mineral acids, including carbonic acid, but less readily by sulphuric acid than by the others. When strongly heated it evolves water and oxygen gas. As diluted nitric acid appeared to decompose this salt without the formation and evolution of any but oxygen gas, I selected this acid as the agent of analysis.

Having procured a very thin light flask with a long narrow neck of the capacity of about four fluid ounces, it was about half filled with dilute nitric acid, which, together with the flask, weighed 1862.05 grs., to this 33.16 grs. of the red barytic salt were gradually added, a rapid evolution of oxygen ensued with every addition of the barytic ferrate; at the expiration of twenty-four hours the flask and contents were weighed = 1891.94 grs., which indicates a loss of 3.27 grs. of oxygen gas; the solution was of a light pink colour, showing that decomposition was not wholly effected; but this entirely disappeared, and the solution became colourless on the addition of two drops of weak hydrochloric acid to the warm solution, evidencing so small an amount of the undecomposed salt as not to be worth considering: this solution evaporated to dryness, redissolved, and filtered, gave 2.78 grs. of silica and sulphate of barytes. On the addition of sulphate of soda to the solution sulphate of barytes was precipitated, which, washed, dried and ignited, weighed, exclusive of ash of filter, 24.64 grs.; the oxide of iron precipitated by ammonia gave 8.88 grs., leaving 2.09 for water and loss.

A second experiment upon a portion of this salt, prepared

at a subsequent period to that used in the first experiment, and adapting a tube containing chloride of calcium to the flask, gave from 47·47 grs. of the compound, 4·31 grs. of oxygen, and, exclusive of ash of filters, 0·48 grs. of silica, &c., 37·82 grs. sulphate of barytes, and 15·27 grs. of sesquioxide of iron, leaving 2·63 grs. for water and loss.

A third experiment gave 3·06 grs. oxygen, ·69 grs. of silica, &c., 27·163 grs. sulphate of barytes, and 10·86 of oxide of iron from 34·47 grs. of the red barytic salt.

To obtain the water, I merely heated the ferrate gradually and gently on a sand heat till it assumed a greenish colour, rejecting those experiments which were partially converted into a light drab colour, which is an evidence of loss of oxygen. 64·48 grs. of ferrate lost 4·93 grs., and 44·41 lost 2·91 grs.; by ignition this green residue was converted into a drab-coloured powder, apparently with the loss of half an equivalent of oxygen, which residue, treated with dilute nitric acid, evolved oxygen gas. Now, estimating the loss sustained in these experiments as water and taking the mean, ferrate of barytes when pure will contain 7·2 per cent. of water, and the three analyses of this barytic salt should respectively indicate, if the loss sustained in these be only water, 2·18 grs. 3·38 grs., and 2·44 grs., a result, as will be seen by reference, so near the loss sustained in analysis, that the difference may fairly be reckoned as merely an error of experiment. The results obtained from the three foregoing analyses, reckoning the loss as water and deducting the silica and sulphate of barytes as impurities, will give respectively 30·38 grs., 46·99 grs., and 33·78 grs., as the quantities of pure ferrate of barytes operated upon, yielding—

	I.	II.	III.
Barytes	16·14	24·78	17·75
Sesquioxide iron .	8·88	15·27	10·77
Oxygen	3·27	4·31	3·06
Water and loss .	2·09	2·63	2·20
	<u>30·38</u>	<u>46·99</u>	<u>33·78</u>

The mean of which will give 19·56 of barytes, 11·64 of sesquioxide of iron, 3·35 of oxygen, and 2·31 of water contained in 37·06 of ferrate barytes.

The 11·64 parts of sesquioxide of iron are composed of 8·15 of iron and 3·49 of oxygen, which uniting with the 3·55 of oxygen gas (within ·06 of a grain in 37·06 grs. of the quantity theoretically required), will yield 15·19 of teroxide of iron, or ferric acid, combined with 19·56 parts of barytes, indicating the formula $\text{BaO FO}_3 \text{HO}$ as the composition of this salt.

Composition of an Acid Oxide of Iron.

247

	Exp.	Theory.
1 equiv. barytes . .	19·56	20·60
1 equiv. ferric acid .	15·19	14·06
1 equiv. water . .	2·31	2·4
	<hr/> 37·06	<hr/> 37·06

I therefore consider the acid oxide of iron present in the deep amethystine solution of the potash salt, and in combination with barytes in the crimson-red barytic salt, to be a teroxide of iron, containing twice the quantity of oxygen existing in the sesquioxide. Whether the pink salt obtained by the agency of chlorine is another and distinct combination of iron with oxygen, forming a still more highly oxygenated compound than ferric acid, I am at present unable to state, but I am inclined to this opinion; it is certain, however, that another acid oxide of iron exists, probably of a lower degree of oxidation than the ferric acid. The combination of this acid with potash or soda is of a beautiful emerald-green colour, precisely similar to the green manganate of potash. The conditions requisite to procure this compound I am at present unable to point out, but I have generally succeeded when I have employed one-half the quantity of nitrate of potash, or what I am inclined to think superior, nitrate of soda, employed to prepare the amethystine salt, and exposed the mixture to a somewhat higher temperature. I have never obtained it unmixed with the purple salt, but owing to its being a much more stable compound than that is, it remains for a considerable length of time undecomposed at ordinary and even elevated temperatures, if excluded from the air. This furnishes an easy method to prove the green salt free from the amethystine salt. Its properties appear analogous to those of the amethystine salts, except with respect to its permanency; acids liberate oxygen, changing the solution to pink, which gradually disappears; chlorine rapidly converts it into the pink salt. It is capable of filtration without being entirely decomposed, but long contact with organic matters appears to resolve it into oxygen and sesquioxide of iron. I regret that at present I have not been able to obtain this green acid of iron in such a state of combination that I can accurately determine its position, but I hope during the next session of the Chemical Society to lay before its members a more detailed investigation of the pink chlorinated compound, and also of the green oxide, and to ascertain their composition and properties.

Romford.