XLII. *On the Action of Oil of Vitriol upon Ferrocyanide of Potassium.* By G. FOWNES, Ph.D.

Read March 21, 1843.

WHEN finely powdered ferrocyanide of potassium is heated in a capacious flask or retort with eight or ten times its weight of concentrated sulphuric acid, the white pasty mass first produced by the action of the acid upon the salt, gradually dissolves and disappears, its solution being accompanied by the disengagement of a prodigious quantity of permanent gas. This gas when collected over water is colourless and transparent; it has a very faint garlic odour, does not render lime-water turbid, takes fire on the approach of a taper, and burns with a bright blue flame, generating carbonic acid. When mixed with half its bulk of pure oxygen, introduced into the siphon-eudiometer and fired by the electric spark, a contraction occurs amounting to one-third part of the whole, and the residual gas becomes almost entirely absorbable by caustic potash. These characters are sufficient to prove that the gas in question is pure carbonic oxide.

When the oil of vitriol is first poured upon the ferrocyanide, a good deal of heat is produced, and the odour of hydrocyanic acid is for a moment perceptible; this disappears, however, as soon as the effervescence commences, and is replaced by a trace of formic acid vapour, which may be remarked during the whole period of the experiment. At the close of the reaction a little sulphurous acid also may be recognised; the cause of this will become immediately apparent.

If, the disengagement of carbonic acid having ceased, heat be still applied to the now fluid contents of the vessel, the escape of sulphurous acid becomes more and more marked, while at the same time a number of little white pearly crystalline plates may be observed floating about in the boiling liquid. These scales rapidly increase in number until, after the lapse of fifteen or twenty minutes from the time the first were seen, they cover the bottom of the flask to a considerable depth, glittering, when agitated, like new-formed crystals of thionurate of ammonia.

When the whole has cooled, the acid may be poured from the crystalline deposit, and the latter washed once or twice by decantation with cold water and then transferred to a paper filter. When the liquid which passes tastes no longer *strongly* acid and astringent, the filter and its contents may be spread upon a few folds of bibulous paper and placed to dry over a surface of sulphuric acid in the vacuum of the air-pump.

The acid liquid from which the crystals were deposited, is found on examination to contain in solution peroxide of iron and the sulphates of potash and ammonia.

The new substance when dry presents a very beautiful appearance, resembling, as before remarked, thionurate of ammonia; under the microscope it is seen to consist of small transparent 6-sided tables. It may be heated to above 300° F. without loss of weight or alteration of any kind; at a red heat it is slowly decomposed, leaving red oxide of iron with some sulphate of potash. It is, as the mode of preparation shows, insoluble in cold water, nevertheless a lengthened sojourn in contact with that liquid brings about slow decomposition; a little free sulphuric acid prevents this change; hence in preparing the substance, the necessity of avoiding prolonged washing, even with cold water, as the salt begins to change and grow red as soon as the free acid has been removed. With boiling water the change is immediate; the substance assumes the colour of rust, and peroxide of iron is dissolved out. Alkalies decompose it instantly, oxide of iron, retaining the crystalline appearance of the new body itself, is separated, and the solution after filtration is found to contain abundance of sulphuric acid. Carbonate of potash with the aid of heat disengages ammonia; the oxide of iron is not in this case separated, but remains in solution, communicating to the alkali a deep red colour; the addition of water, however, causes the deposition of the oxide. These characters suffice to point out the general nature of the substance under examination.

A portion carefully dried *in vacuo* was next subjected to analysis:—

20 grs. dissolved in hot hydrochloric acid and precipitated by ammonia gave 6 grs. of oxide of iron, and the filtered solution, evaporated to dryness and ignited with the usual precautions, afforded 2·9 grs. of sulphate of potash, equivalent to 1·58 grs. of potash.

20 grs. of the substance, dissolved in hydrochloric acid and precipitated by chloride of barium, gave 34·4 grs. of ignited sulphate = 11·8 grs. of sulphuric acid.

20 grs. of the substance, digested with ammonia and filtered, gave of oxide of iron 5·9 grs.; the solution by precipitation with baryta afforded 34·2 grs. of sulphate = 11·74 grs. of sulphuric acid.

100 parts will therefore contain, if the ammonia be taken by difference,—

Sulphuric acid . . .	59·0	58·7
Peroxide of iron . . .	30·0	29·5
Potash	7·9	
Oxide of ammonium . .	3·1	
	100·0	

A separate specimen, the result of another operation, gave numbers closely coinciding with the above.

It will be seen that the relation of the sulphuric acid to the oxide of iron is almost exactly that which exists in common iron-alum; the formula

gives, reckoned to 100 parts,—

Sulphuric acid	58·0
Peroxide of iron . . .	28·8
Potash	8·5
Oxide of ammonium . .	4·7
	100·0

Taking into account the impossibility of completely washing the crystals without causing decomposition, a comparison of the calculated and found results will perhaps be deemed satisfactory.

This anhydrous iron-alum is apparently the type of a number of crystalline anhydrous sulphates which may be formed under similar circumstances. For example, when green vitriol in powder is boiled with strong sulphuric acid it is dissolved, sulphurous acid is disengaged, the protoxide of iron passing to peroxide, which, as fast as it is formed, falls down in combination with the acid as a crystalline pinkish-white powder.

Anhydrous sulphates of copper and nickel may be obtained by a similar process ; also the double sulphate of nickel and potash. The copper salt has a beautiful lilac colour ; that of nickel is bright yellow. All these compounds are, however, changed by contact with water ; the persulphate of iron is the most stable, but even that ends by dissolving in great part.

There is no difficulty in explaining the decomposition undergone by the ferrocyanide of potassium under the influence of the acid, and its conversion into the products observed.

1 equivalent of ferrocyanide of potassium and 9 equivalents of water contain the elements of 6 equivalents of carbonic oxide, 3 equivalents of ammonia, 2 equivalents of potash, and 1 equivalent of protoxide of iron.

1 eq. ferrocyanide potassium =	{	6 eq. carbon.	6 eq. carbonic oxide.
		3 „ nitrogen.	
		2 „ potassium.	2 eq. potash.
		1 „ iron.	1 eq. protox. iron.
9* eq. water. . . . . =	{	6 „ oxygen.	
		2 „ oxygen.	
		1 „ oxygen.	
		9 „ hydrogen.	3 eq. ammonia.

At a subsequent period, when the evolution of carbonic oxide ceases and the temperature rises very high, the iron becomes peroxidized at the expense of a portion of the acid, sulphurous acid is emitted, and the iron-alum gradually formed, the excess of alkaline sulphates remaining in solution.

In conclusion, it may be worth while calling the attention of those whom it may concern to the foregoing experiments, as furnishing an extremely easy and economical method of preparing carbonic oxide for purposes of research or demonstration. A single half-ounce of the yellow salt treated with some oil of vitriol in a common Florence flask fitted with a perforated cork and conducting tube, gives more than 300 cubic inches of gas, which has all the marks of the most perfect purity : it does not in the least affect lime-water, and becomes entirely converted into carbonic acid by explosion with half its volume of oxygen. The gas given off during the whole of the reaction is equally pure, except quite at the end of the operation, when, as before noticed, a little sulphurous acid appears.

* Probably 6 eq. from the oil of vitriol, the acid of which has combined with the ammonia, potash and oxide of iron, and 3 eq. being the water of crystallization of the salt.