XX. *On the separation of Iron from other metals.* *By* J. F. W. Herschel, *Esq. F. R. S.*

Read April 5, 1821.

An easy and exact method of separating iron from the other metals with which it may happen to be mixed, has always been a desideratum in chemistry. Every one conversant with the analysis of minerals is aware of the difficulty of the problem, which indeed is such that, in experiments conducted on any thing like a large scale, it might hitherto be regarded as insuperable. In consequence of this, and of the importance of the enquiry, there is hardly a chemist of eminence who has not proposed some process for the purpose, but (with the exception of that which depends on the insolubility of the persuccinate of the obnoxious metal, which I have not tried, and which is too expensive to be resorted to for any but the nicer purposes of analytical research) they are all of them either inadequate to the end proposed, intolerably tedious, or limited in their application. That which I have now to propose, on the other hand, is liable to none of these objections, being *mathematically* rigorous, of general application, and possessing in the highest degree the advantages of facility, celerity, and cheapness. It is briefly this:

The solution containing iron, is to be brought to the maximum of oxidation, which can be communicated to it by boiling with nitric acid. It is then to be just neutralized *while in a state of ebullition*, by carbonate of ammonia. The whole of the iron to the last atom, is precipitated, and the whole of the other metals present (which I suppose to be manganese, cerium, nickel, and cobalt), remains in solution.

The precautions necessary to ensure success in this process are few and simple. In the first place, the solution must contain no oxide of manganese or cerium above the first degree of oxidation, otherwise it will be separated with the iron. It is scarcely probable in ordinary cases that any such should be present, the protoxides only of these metals forming salts of any stability; but should they be suspected, a short ebullition with a little sugar will reduce them to the minimum. If nitric acid be now added, the iron alone is peroxidized, the other oxides remaining at the minimum.* Moreover, in performing the precipitation the metallic solution should not be too concentrated, and must be agitated the whole time, especially towards the end of the process; and when the acid reaction is so far diminished that log-wood paper is but feebly affected by it, the alkaline solution must be added cautiously, in small quantities at a time, and in a diluted state. If too much alkali be added, a drop or two of any acid will set all right again; but it should be well observed, as upon this the whole rigour of the process depends, that no inconvenience can arise from slightly surpassing the point of precise neutralization, *as the newly precipitated car-*

---

* Dr. FORSCHAMMER, in a paper recently published in THOMSON'S Annals of Philosophy, contends that the proto-salts of manganese are absolutely void of colour. To this I can only say, that I have not succeeded in depriving the muriate of its pale rose colour by any length of ebullition with sugar or alcohol, after which, however, not a trace of deutoxide could be detected in it. I cannot help regarding the process here proposed for freeing manganese from iron as preferable to that of Dr. F.

bonates of the above enumerated metals are readily soluble, to a certain extent, in the solutions in which they are formed (though perfectly neutral). In the cases of cobalt and cerium, this re-dissolution of the recent precipitate formed by carbonate of ammonia is very considerable, and a solution of either of these metals, thus impregnated with the metallic carbonate, becomes a test of the presence of peroxide of iron, of a delicacy surpassing most of the re-agents used in chemistry, the minutest trace of it being instantly thrown down by them from a boiling solution, provided no marked excess of acid be present. To be certain however that we have not gone too far, it is advisable, after separating the ferruginous precipitate, to test the clear liquid, while hot, with a drop of the alkaline carbonate. If the cloud which this produces be clearly re-dissolved on agitation, we may be sure that only iron has been separated. If otherwise, a little acid must be added, the liquor poured again through the filter, so as to wash the precipitate, and the neutralization performed anew.

The precipitation of iron above described seems at first sight to result from a double decomposition. Were it so, the principle of the method would be merely a difference of solubility in the carbonates of iron and the other metals, and as such would have no claim to be regarded as rigorous. Such however is not the case. The iron is not separated in the state of a carbonate, but of a sub-salt, or a simple peroxide, the whole of the carbonic acid escaping with effervescence at each addition of the alkali. The phænomenon turns on a peculiarity in the peroxide of this metal, in virtue of which it is incapable of existing in a neutral solution at the boiling temperature. If we add an alkaline, earthy, or metallic carbonate by little and little to a *cold* solution of peroxide of iron, the precipitate formed is re-dissolved with effervescence, readily at first, but gradually more and more slowly, till at length many hours, or even days, elapse before the liquid becomes quite clear. Meanwhile it deepens in colour till (unless much diluted) it becomes dark brown or red. If the addition of the carbonate be carried as far as possible without producing a permanent precipitate, the solution is perfectly neutral, and continues clear at a low temperature for any length of time. In this state it may be evaporated to dryness in *vacuo*, and the residue (which *does not effervesce* with acids) is still soluble in water without letting any iron fall, and so on as often as we please.

The compound thus formed is however far from permanent. It is in fact in a state of tottering equilibrium, which a very slight cause is sufficient to overset. Supposing the point of saturation to have been exactly attained, the addition of an extremely small quantity *more* of the alkaline solution is sufficient to determine the separation of the whole, or nearly the whole, metallic contents; and if the solution operated on be pretty concentrated, it fixes after a longer or shorter time into a stiff and almost solid coagulum. Again, if to the coagulum so formed, a quantity equally inappreciable of the original ferruginous solution be added, it gradually liquefies, and after some time is completely re-dissolved (forming no inapt representation of the celebrated imposture of St. Januarius's blood)*

---

* The phænomenon described in the text appears to me to differ from ordinary precipitations and solutions, in the small proportion between the precipitant and the

A similar change is produced by an increase of temperature. If we heat a solution exactly neutralized as above described, it speedily grows turbid, deposits its ferruginous contents in abundance, *and at the same time acquires a very decided acid reaction.* The acid so developed holds in solution a portion of oxide, but if the neutralization be performed afresh *while hot,* this separates entirely, and the liquid after filtration has no more action on gallic acid, ferrocyanate, or sulphocyanate of potash, than so much distilled water.*

It is not my object in this paper to enter into any minute detail of the nature of the persalts of iron, a subject not nearly exhausted, and which want of leisure alone has prevented my entering upon, but merely to point out the practical application of this one of their properties, to an important

precipitate, the solvent and the matter dissolved. I can call to mind but one instance of so small a quantity of matter operating a chemical change on so large a mass, *viz:* the decomposition of oxygenated water by fibrin and other animal substances. The action seems to be propagated from particle to particle. Whether the superabundant oxide of iron be retained in solution in a state at all analogous to that of the oxygen in THENARD's experiments, might possibly deserve consideration.

* It was in 1815, in the analysis of a specimen of the gold ore of Bakebanya, given me for that purpose by Dr. CLARKE, that I first remarked the separation of oxide of iron from a clear neutral solution by mere elevation of temperature, and attributed it to the presence of an oxycarbonate capable of subsisting in a low temperature, but decomposed by heat. That this is not the true explanation is already shown, and I have considerable doubt of the existence of a percarbonate of iron at *any temperature.*

The most elegant mode of exhibiting the experiment is perhaps the following: having rendered a solution of proto-sulphate of iron rigorously neutral, by agitation with carbonate of lime and filtration, dissolve in it a small quantity of chlorate of potash (a salt perfectly neutral). The solution when raised to ebullition is peroxidized, a quantity of sub-sulphate precipitates, and the supernatant liquid is found decidedly, and even strongly acid.

object in analysis. The principle here developed furnishes a ready method of detecting the minutest quantities of other metals in union with iron, and therefore cannot but prove of important service in various cases where this metal constitutes the chief ingredient in the substance examined, as in meteoric iron, the various natural oxides of this metal, &c. &c. I will exemplify this in one or two instances.

36·00 grains of meteoric iron (furnished me by the kindness of Dr. Wollaston) were dissolved in dilute nitrosulphuric acid, leaving behind a minute quantity of a brilliant black powder, which however dissolved by digestion in nitromuriatic acid, and appeared only to contain an excess of nickel. The solutions were mixed, and being neutralized at a boiling temperature by carbonate of ammonia, and the iron separated, a green solution remained. Into this when boiling, a drop of persulphate of iron being let fall, was immediately precipitated in the state of subsulphate, which being separated, the solution was boiled with excess of caustic potash till all smell of ammonia disappeared. Oxide of nickel separated, which collected and strongly ignited, weighed 4·65 grains, or 12·92 on the hundred, which (taking the atom of nickel to weigh 30, and that of oxygen 8, hydrogen being unity) gives 10·20 per cent for the contents of the specimen analyzed in metallic nickel.

100 grains of titanious iron from North America, being dissolved in muriatic acid (after the requisite ignition with potash) were treated (after separating the titanium) with excess of carbonate of lime and filtered. The excess of carbonic acid being expelled, ammonia was added, and a small quantity of a white precipitate fell, which speedily blackened

in the air, and proved to be mere oxide of manganese, uncontaminated by iron, and amounting to half a grain.

Manganese has been suspected in various species of cast iron; and though Mr. MUSHET's experiments go to prove that it does not usually enter in abundance, they can hardly be regarded as establishing the fact of its absence. It might not be uninteresting to resume the investigation with the aid of a mode of analysis so well adapted to experiments on a large scale, as I have no doubt that, with proper care, one part in a thousand, or even less, of manganese might be insulated from iron.

The separation of iron from uranium cannot be accomplished by the process above described, that metal possessing a property analogous to that which forms the subject of this paper. By inverting the process, however, we shall succeed even here. A mixed solution of iron and uranium being de-oxidized by a current of sulphuretted hydrogen, and then treated with an earthy carbonate, the iron passes in solution while the uranium separates. This difference in the habitudes of the two oxides of iron presents us in fact with a kind of chemical dilemma, of one or the other of whose horns we may avail ourselves in any proposed case. In studying the habitudes of uranium, however, I have met with some anomalies which require farther investigation. Zirconia too might probably be freed from iron with equal facility by a similar inversion of the process; but this I have not yet had an opportunity of trying satisfactorily.

J. F. W. HERSCHEL.

London,
April 4, 1821.