

XXVI. *On the Nature of the Salts termed triple Prussiates, and on Acids formed by the union of certain Bodies with the Elements of the Prussic Acid.* By Robert Porrett, jun. Esq. Communicated by William Hyde Wollaston, M. D. Sec. R. S.

Read June 30, 1814.

SINCE the admirable experiments of SCHEELE on the Prussic acid, chemists have distinguished between the salts formed by the direct combination of this acid with alkaline or other bases, and those obtained either by adding to the salts just mentioned a certain portion of a metallic oxide, or by decomposing by the alkalies a prussiate of a metallic oxide. Thus for instance, the salt formed by the union of the Prussic acid with potash has been called the simple prussiate of potash, while that obtained by boiling a solution of potash on Prussian blue has been called the triple prussiate of potash and iron, it having been proved that the black oxide of iron enters into its composition. The differences between these salts are very remarkable, the simple prussiate is always alkaline, is soluble in alcohol, is incapable of forming Prussian blue when added to the salts of per-oxide of iron, gives a yellow precipitate with salts of per-oxide of copper, is decomposed at the temperature of boiling water, and has its acid displaced by the carbonic acid. On the contrary, the triple prussiate is neutral, is insoluble in alcohol, forms Prussian blue with the salts of per-oxide of iron, gives a reddish brown precipitate with salts of per-oxide of copper,

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is not decomposed at the boiling temperature, nor in the least altered by carbonic acid. To the black oxide of iron, therefore, existing in this salt, chemists have attributed its superior permanency to the simple prussiate, and also its conversion to the neutral state. The latter effect of the oxide of iron is without a parallel in chemistry, no other alkaline salt is known which can be rendered neutral by the mere addition of black oxide of iron, which in all other instances will neutralize acids instead of alkalies. This however is not the only anomaly which the triple prussiates present, the following being also very remarkable.

The black oxide of iron contained in them cannot be thrown down by the addition of any of the hydrosulphurets, succinates, gallates, or any other tests for iron.

This oxide always accompanies the Prussic acid, when the latter is transferred by stronger affinities from one base to another.

For most of the facts just related, I am indebted to the excellent paper of PROUST, entitled "Facts towards a History of the Prussiates." It appeared to me to be necessary to restate these facts in order to render clear the objects of this communication, which are to reconcile with the general properties of other saline bodies the anomalies which the triple prussiates present; to simplify the received opinion respecting their nature, and to make known some new acids which I have discovered.

In endeavouring to accomplish these objects, I shall first state my opinion of the nature of the triple prussiates as they are called, and afterwards support it by experiments.

I consider the salts termed triple prussiates as binary com-

pounds of an acid with a single base; as salts which do not contain any Prussic acid, nor any oxide of iron *as a base*, although both these substances may be obtained from them by a decomposition of their acid.

The first experiment which I shall adduce in support of the above opinion is one with the Voltaic battery; it appeared to me that this instrument would shew whether the oxide of iron in the triple prussiates existed in them as a base, or as an element of a peculiar acid by attracting it to the negative pole in the former, and to the positive pole in the latter case. I therefore exposed a solution of triple prussiate of soda to the agency of a small battery of fifty pair of double plates of one inch and a quarter square, kept in action for twenty hours, the solution was connected by platina wire with the negative pole, and by filaments of cotton with distilled water which communicated by platina wire with the positive pole. Thus circumstanced the triple prussiate of soda was decomposed, its acid (consisting of the elements of prussic acid and black oxide of iron) was carried over to the positive pole; here, meeting with oxygen from the decomposing water, it underwent a farther change by which it was converted into Prussic acid which was partly volatilized, and into blue triple prussiate of iron which formed there in abundance; the liquid at the negative pole after this process contained only soda with a trace of undecomposed triple prussiate. In this experiment I consider the circumstance of the black oxide of iron being carried over to the positive pole as a proof that it went there as an element of an acid, for as a base it must have remained at the negative pole.

I have repeated the above experiment with only the variation

of employing conducting wires of copper instead of platina, and found that the only difference in the result was, that the reddish brown triple prussiate of copper and iron was formed instead of the blue triple prussiate of iron, which effect was owing to the oxide of copper formed at the positive pole combining with the peculiar acid of the triple prussiates.

The next experiment which I shall relate is still more conclusive. I dissolved the triple prussiate of barytes in cold water, of which it required 1800 times its weight, I divided this equally, and by an experiment made purposely with one portion, ascertained the exact quantity of diluted sulphuric acid necessary to throw down the barytes from the other; this quantity was equal to 2,53 grains of real sulphuric acid for every ten grains of the salt employed; then filling a bottle with the second portion so as only to leave room for the acid to be added, I poured into it the quantity of acid previously ascertained, closed the bottle immediately, and left the sulphate of barytes to subside to the bottom; when this had taken place, the clear supernatant fluid was examined, and found to be the pure acid of the triple prussiates. It has the following characters:

It is of a pale lemon yellow colour; it has no smell; it is decomposed by a gentle heat, or by exposure to a strong light; prussic acid is then formed, and white triple prussiate of iron, which quickly absorbing oxygen from the air, changes to blue triple prussiate. It forms directly with alkalis, earths, or oxides, the salts termed triple prussiates. It displaces the acetic acid from all its combinations in the cold, and forms triple prussiates with the bases before united to that acid. It is capable of expelling all other acids from their soluble

combinations, when it can form with their bases compounds that are insoluble in acids.

The decomposition of the abovementioned peculiar acid by heat, shews the reason why the acid of the triple prussiates can never be obtained from them by distilling these salts with a stronger acid, and why in these cases, Prussic acid and triple prussiate of iron are always obtained.

By proving that the oxide of iron contained in the triple prussiates is an elementary part of an acid *sui generis*, the several anomalies mentioned in the beginning of this Paper are easily explained, for instance, its occasioning the simple prussiates to pass from an alkaline to a neutral state, is owing to its constituting with the other elements present, a new acid having much stronger acid properties than the Prussic. Its not being affected by the usual tests for iron is owing to its existing as an element of an acid, in which state it is no more to be expected that it should be discovered by the ordinary reagents, than that the sulphur in sulphuric acid should blacken metallic solutions. Finally, its accompanying the elements of the Prussic acid in all cases of transfer from one base to another, is owing to its forming with these elements the acid of the triple prussiates, which acid, when transferred by stronger affinities, carries with it of course all its component parts. I have discovered that besides the black oxide of iron there are other substances which are capable of forming, with the elements of Prussic acid, peculiar acids having properties widely different from each other.

Sulphur is one of these substances.

Several of the metallic oxides, I have reason to think, are

also of this kind, but I have not had leisure to investigate particularly the acids that may thus be formed.

That with sulphur however has engaged much of my attention, as may be seen by reference to the continuation of this Paper.

The true nature of the triple prussiates being, as I hope, now developed, an alteration in their nomenclature appears indispensable, as those salts can no longer with propriety be called triple salts which have but one acid and one base, nor can they be called prussiates which do not contain any prussic acid. Besides, it seems full time that the term prussiates should be restricted to the simple compounds of Prussic acid with bases, and that salts so very different from them, as are the triple prussiates, should have a name so dissimilar as to prevent for the future any farther confusion between them; I propose therefore for the acid composed of the elements of the Prussic acid united with oxide of iron, the name of ferruretted chyazic acid, for that composed of the same elements with sulphur the name of sulphuretted chyazic acid, for those consisting still of the same elements with metallic oxides analogous names, as argenturetted chyazic acid, &c. the word chyazic being composed of the first letters of the acidifiable elements of the acid, viz. carbon, hydrogen, and azote, to which is added the termination *ic*.

I shall now relate some analyses that I have made of the triple prussiates, or as I shall henceforth call them, the ferruretted chyazates.

*Analysis of ferruretted Chyazate of Potash. (Triple Prussiate of Potash.)*

I cannot find that this salt has ever been completely analysed: the only person who to my knowledge has even partially effected it is PROUST, who confined himself to ascertaining the quantities of water and of black oxide of iron which it contains, and which he states to be in the 100 parts,

Water	-	10
Black oxide of iron		17

I have made similar experiments to those from which he drew the above conclusions, and added others of my own; the following are the particulars of these experiments with the results which I have obtained.

A. 100 grains of the crystallized salt, finely pulverized, were kept for six hours at the temperature of  $212^{\circ}$ , by this treatment they were reduced in weight thirteen grains; they were afterwards heated for one hour at the temperature of  $40^{\circ}$ , but they did not suffer any further loss.

B. 100 grains of the same salt were heated with weak sulphuric acid until all the Prussic acid that could be expelled as gas was separated, the rest of the Prussic acid combined during the process with the oxide of iron contained in the salt, and formed ferruretted chyazate of protoxide of iron (white prussiate of iron), which I afterwards changed into ferruretted chyazate of per-oxide of iron (blue prussiate of iron) by the addition of a little weak nitric acid; it was then thoroughly washed and dried at  $212^{\circ}$ , it weighed after this thirty-five grains. These thirty-five grains, as may be seen by the analysis which I have made of the ferruretted chyazate of

per-oxide of iron by its combustion, which will be related presently, contain 6.76 grains of black oxide of iron and 11.71 grains of red oxide of iron, but as the whole of the iron in the ferruretted chyazate of potash is in the state of black oxide, these 11.71 grains of red oxide must be reckoned as 10.5 grains of black oxide, which added to the 6.76 grains gives 17.26 as the quantity of black oxide of iron contained in 100 grains of the ferruretted chyazate of potash.

C. 100 grains of crystallized ferruretted chyazate of potash dissolved in water and poured into a solution of green sulphate of iron gave a precipitate which, treated exactly as the last, was ferruretted chyazate of per-oxide of iron and weighed 89.3 grains, the elements of the Prussic acid contained in which weigh 30.4 grains, as may be seen in the analysis before referred to.

D. 100 grains of the same crystallized salt, decomposed by sulphuric acid, gave a quantity of sulphate of potash which, after fusion in a platinum crucible by a strong red heat, weighed 78.5 grains : now as 100 grains of sulphate of potash in this state contain, according to Dr. THOMSON (*Annals of Philosophy* for Oct. 1813), 50.1 grains of potash, therefore these 78.5 grains must have contained 39.33 of that alkali.

Hence, neglecting minute fractions, the crystallized ferruretted chyazate of potash is composed of

Grains.	Water A	-	-	-	-	Grains.	
						13.00	
17.26	black oxide of iron B	}	ferruretted chyazic	acid	-	}	47.66
30.40	elements of Prussic acid C						
	Potash D	-	-	-	-	39.34	
						100.00	



*Analysis of ferruretted Chyazate of Barytes.* (Triple Prussiate of Barytes.)

A. 100 grains of this salt exposed to the temperature of 340° until they no longer lost weight, parted with 16.59 grains of water.

B. 10 grains of the salt were added to about eight ounces of water acidulated with muriatic acid to increase its solvent power on the salt; when the whole was dissolved, a solution of supersulphate of potash was poured into it as long as it occasioned any precipitate, this precipitate after having been well washed, dried, and ignited in a platinum crucible, weighed 7.44 grains, which, according to BERZELIUS's analysis of sulphate of barytes, contain 4.91 grains of barytes.

C. As this salt consists only of ferruretted chyazic acid with barytes and water, the quantity of the two last being ascertained leaves for the other in the 100 grains, 34.31 grains.

100 grains of ferruretted chyazate of barytes is therefore composed of

Water A	-	-	-	-	16.59
12.42 Black oxide of iron	}	ferruretted chyazic	acid C	-	} 34.31
21.89 Elements of Prussic acid					
Barytes B	-	-	-	-	49.10
					100.00
					100.00

*Analysis of ferruretted Chyazate of Per-oxide of Iron.* (Blue Prussiate of Iron.)

A. I found that in order to form 100 grains of ferruretted chyazate of per-oxide of iron, it was necessary to add 112

grains of ferruretted chyazate of potash to a solution of iron; now by my analysis of this salt, it appears that the quantity of acid in these 112 grains is 53.38 grains, the whole of which acid enters into the composition of the 100 grains of blue precipitate.

B. 124 grains of crystallized green sulphate of iron being dissolved in water, there was required to precipitate all the oxide of iron from it, a solution containing 112 grains of crystallized ferruretted chyazate of potash; now 124 grains of crystallized green sulphate contain, according to BERZELIUS, 31.44 grains of protoxide of iron, but as this iron is in the state of per-oxide in Prussian blue, it must be reckoned as 35 grains.

C. PROUST has stated that the quantity of per-oxide of iron procured by calcining 100 grains of Prussian blue is 55 grains, I have repeated this experiment and obtained the same result; of these 55 grains, 21.53 grains must have been derived from the 53.38 grains of acid in the Prussian blue (see Exp. A), in which they existed as black oxide, weighing only 19.33 grains.

D. I attempted to obtain by distillation the water that is contained in Prussian blue, that had been dried as much as possible at 212° by heating 100 grains of it at the temperature of melting tin in a small retort adapted to a receiver containing fused muriate of lime, the retort and the receiver with their contents being separately weighed, both before and after the experiment; but I found that only an approximation to the truth could be gained by this method, as the water that came over held prussiate of ammonia in solution, and as some of the same prussiate escaped as gas: after the experiment

I found that the contents of the retort had lost in weight 19.5 grains, and that those of the receiver had gained 10.5, the mean between these two is 15 grains, which does not differ very materially from the quantity deduced from ascertaining the weight of all the other constituents of Prussian blue, consequently this latter method may be adopted without the hazard of any material error.

Ferruretted chyazate of per-oxide of iron according to these experiments is composed of

19.33 Black oxide of iron	}	Ferruretted chyazic	
34.05 Elements of Prussic acid	}	acid A	53.38
		Per-oxide of iron B	35.00
		Water D	11.62
			100.00

or if its composition be calculated from the quantity of per-oxide of iron afforded by its combustion, jointly with the quantity of ferruretted chyazate of potash required to form it, then it will consist of

Ferruretted chyazic acid A	-		53.38
Per-oxide of iron C	-		33.47
Water D	-		13.15
			100.00

These analyses by different methods agree together as nearly as could well be expected, the mean of the two is given below, which cannot, I think, be far from the truth.

Ferruretted chyazic acid		53.380
Per-oxide of iron	-	34.235
Water	- -	- 12.385
		<hr/>
		100.000
		<hr/>

Before I dismiss the subject of the ferruretted chyazates, I beg to make some remarks on the opinion generally entertained by the most eminent chemists, of the inadequacy of these salts as tests for iron capable of affording correct information of the *quantity* of oxide of iron that may be present in a solution : in doing which I hope to shew that this opinion is erroneous.

*Remarks on the objections made to the use of the ferruretted Chyazate of Potash as a test for the quantity of Iron in Solutions.*

These objections I find very well stated by Dr. MARCET, in his Chemical Account of an aluminous Chalybeate Spring in the Isle of Wight, as follows :

“ The prussiate of pôtash, however well prepared, is quite  
 “ inappropriate when the object is to ascertain the *quantity* of  
 “ iron in solution, its utility being confined to indicating its  
 “ presence, it being liable to the objections of precipitating  
 “ some earthy substances, particularly alumine, when the mix-  
 “ ture is heated, of being itself decomposed by heat, or of  
 “ not separating the iron so as to be retained on the filter or  
 “ procured by subsidence, if heat is not applied, or if the iron  
 “ is not highly oxidated.”

Notwithstanding the authority which an opinion of Dr. MARCET's on this subject justly carries with it, I must take the liberty of asserting, that although I agree with him in the

experimental facts cited as the causes for it, yet that I draw a different conclusion from his, because, instructed by my experiments on the nature of the triple prussiates, I find that all those inconvenient effects are easily prevented from ensuing; and I therefore conclude that the ferruretted chyazate of potash is in general the most appropriate test of the quantity of iron in solution of any employed in chemistry; the use of it for this purpose only requiring attention to the following facts.

1st. That if the ferruretted chyazate of potash after being dissolved in water gives immediately a blue precipitate by the addition of muriatic acid, it is not pure, and will give a fallacious result.

2dly. That if this salt, however pure, be added *in excess* to a solution of iron *containing an excess of acid*, and then heated, the Prussian blue thrown down will weigh more than it ought, because some is furnished by the decomposition of the ferruginous acid of that part of the salt which has been added in excess.

3dly. That Prussian blue, even after it has been formed, is materially acted upon by a mixture of nitric and muriatic acids, and in some degree by the muriatic acid alone at a boiling heat.

4thly. That Prussian blue, when precipitated, often carries with it sulphate of potash derived from the liquid from which it is thrown down; and that this sulphate adheres to it so obstinately that several washings with water acidulated with sulphuric acid, are necessary to detach it.

5thly. That if the solution to which the test is applied contains besides iron, barytes, alumine, oxide of copper, or any

other substance which the ferruretted chyazate is known to precipitate, then it is necessary to separate such substance by the usual means, before the application of this test for iron.

With the knowledge of these facts, therefore, it is easy always to obtain correct results, which will best appear by assuming a case particularly unfavourable for the purpose, and shewing how the difficulties of that case may be obviated.

Let it therefore be supposed that the analyst has a solution having a considerable excess of nitromuriatic acid and containing oxide of iron, barytes, alumine, magnesia, and oxide of copper, and that he wishes to precipitate the iron by the ferruretted chyazate of potash. If he first throw down the barytes by a sulphate, then the other earths and oxides by ammonia, adding an excess of ammonia to redissolve the oxide of copper, if he then separate the alumine by digestion in caustic potash, and redissolve the oxide of iron and magnesia in an acid, which for the sake of increasing the difficulty may again be supposed to be the nitromuriatic; I say then, that by neutralizing any very great excess of acid, and adding some acetite of potash in order that the unavoidable excess of acid may be the acetic instead of the nitromuriatic; then applying the ferruretted chyazate of potash, taking care that there be but little, if any, excess of it added; he may safely boil the liquid and readily collect by the filter, or by subsidence, the ferruretted chyazate of per-oxide of iron, which when properly washed, dried, and weighed, will indicate very accurately the quantity of iron that was in the solution, by reckoning that quantity as 34.235 of per-oxide, for every 100 parts of Prussian blue obtained.

The succinates and benzoates which have been proposed as superior tests for determining the quantity of iron, to the ferretted chyazates, I consider to be in general very inferior to them, because they do not precipitate the iron, when it is in the state of protoxide, which the latter do, and because they precipitate alumine more effectually than those salts.

*On sulphuretted Chyazic Acid.*

I discovered this acid in the latter part of the year 1808, whilst engaged in an experiment the object of which was to form prussiate of potash by the mutual action of Prussian blue and sulphuret of potash when boiled together; I found after this boiling had been continued for a considerable time with fresh additions of Prussian blue, until the alkaline liquid was completely neutralized, that instead of prussiate of potash which I had expected to obtain, a new principle had been formed which had properties totally different from the Prussic acid, or from any other known chemical substance. I made experiments in order to separate this principle from the various products which were mingled with it in the liquid which I obtained, and having succeeded in this, I found that in its pure state it had acid properties, and was capable of being converted by oxidizing agents into Prussic acid; this circumstance considered in conjunction with its being formed by a deoxidating process on a salt of iron containing the Prussic acid, led me to conclude, that this new acid differed from the Prussic acid only in containing less oxygen, I therefore named it Prussous Acid, and in a paper which I presented to the Society of Arts in April 1809, detailed the circumstances of its formation, the mode of obtaining it free from foreign bodies,

and its effects on many of the metallic solutions. Since the experiments were performed which I then communicated, I have made several others which have added considerably to my knowledge of the nature and properties of this peculiar acid, and proved to me that my first opinion of its nature was incorrect. I shall endeavour in this paper to give as concise an account of these experiments as I am able, consistently with making myself understood, notwithstanding which I fear that from their number it will not be in my power to compress them within moderate limits; in attempting this, however, I shall arrange them under the following heads:

- 1st. Experiments on this acid of a synthetical nature.
- 2dly. Experiments on the same of an analytical nature.
- 3dly. Experiments on the salts formed by this acid.

Before I detail the experiments of the first and second class which relate to the nature of this acid, I beg to observe that in describing them I shall designate this acid provisionally by the name of the red tinging acid, as neither the name of Prussous acid, which I first gave to it, nor that of sulphuretted chyzic acid, which I now adopt, could in this place be used with propriety, as they each imply different compositions of this acid, the true nature of which, until these experiments are related, must be presumed to be doubtful.

#### *Synthetical Experiments on the Red Tinging Acid.*

Under this head I shall include not only the different processes by which I have actually formed this acid, but those also by which I have attempted to form it without success, as both kinds of experiments throw light upon its nature; I shall



add also the account of the processes by which I have obtained it pure from the liquid in which it is formed.

*Processes by which I have formed the Red Tinging Acid.*

A. The first is the one already mentioned, which consists in boiling, for a considerable length of time, three or four parts of Prussian blue in powder added at as many intervals, with one part of sulphuret of potash, which sulphuret by the action of the hot water upon it becomes an hydroguretted sulphuret. The products of this process are black sulphuret of iron, and a colourless neutral liquid containing a considerable quantity of the red tinging acid combined with potash, much sulphurous acid in union with sulphur and potash, forming a sulphuretted sulphite of potash, and some sulphate of potash.

B. The second process is analogous to the preceding, it consists in decomposing prussiate of mercury by hydroguretted sulphuret of potash, this decomposition, owing to the solubility of this prussiate, is instantaneous, while the former only takes place after a tedious ebullition; the products of it do not differ in any respect from the former, with the exception, that instead of the black sulphuret of iron, there is formed the black sulphuret of mercury.

C. The third process consists in heating to redness for some hours a mixture of animal charcoal and sulphuret of potash, and, when the mass is cold, lixiviating it with water. This process, which is by far the most economical of any, gives the same results as the former, with the exception of there being no metallic sulphurets, and that the liquid generally contains much undecomposed hydroguretted sulphuret of potash.

D. The fourth process is only a variation of the third, by substituting for the sulphuret of potash, the sulphate of that alkali, which sulphate is converted to sulphuret during the process by part of the animal coal; I performed this process but once, but it did not appear to me to give so large a quantity of the red tinging acid as the last.

E. The fifth process consists in forming the simple alkaline prussiate of potash by passing Prussic acid gas through a solution of that alkali, and afterwards boiling this liquid alkaline prussiate with a little sulphur, the whole of the Prussic acid in this salt is thus changed into red tinging acid.

F. The sixth process is very analogous to the last, it consists in adding to the simple prussiate of ammonia, hydrogenretted sulphuret of potash, by which the simple prussiate of ammonia is immediately changed into the compound of ammonia with the red tinging acid. The liquid after the process always contains sulphuretted hydrogen, even when the hydrogenretted sulphuret has been added in a quantity insufficient to convert the whole of the Prussic acid into red tinging acid.

These are the various processes by which I have formed the red tinging acid, those by which I could *not* form it are now to be mentioned.

G. *Experiment 1.* Ammoniacal gas was passed through a red hot earthen tube containing charcoal, by this process as is well known Prussic acid is abundantly formed, but my object in performing it, was to ascertain whether any of the red tinging acid was at the same time produced; not the slightest trace of it, however, could be detected in any of the products.

H. *Experiment 2.* Phosphuret of lime was thrown into the simple prussiate of ammonia, phosphuretted hydrogen was as usual produced, but no red tinging acid was formed.

I. *Experiment 3.* Phosphuret of lime thrown into prussiate of mercury threw down the mercury as a black powder, the liquid after this contained prussiate of lime, but none of the red tinging acid.

K. *Experiment 4.* Phosphuretted hydrogen gas was passed through prussiate of mercury, the mercury was thrown down, and Prussic acid set free.

L. *Experiment 5.* Arseniuretted hydrogen gas acted in a similar manner.

M. *Experiment 6.* Sulphuretted hydrogen gas passed through the same salt occasioned similar phenomena, black sulphuret of mercury being formed and Prussic acid disengaged.

N. *Experiment 7.* The same gas passed through the simple prussiate of ammonia did not alter that prussiate.

O. *Experiment 8.* 0.5 of a cubic inch of the same gas, at mean temp. and pressure being passed up into a tube over mercury, and an equal volume of Prussic acid gas being added, the volume of the two gases was not altered by the mixture, nor did any combination take place.

P. *Experiment 9.* The preceding experiment was repeated with the addition of passing 150 electric discharges through the two gases, but no combination ensued.

Q. *Experiment 10.* A repetition of Experiment 8, with the addition of 0.5 of a cubic inch of chlorine gas, the volume of the mixed gases was diminished to one-third of their former bulk, and sulphur was deposited on the inside of the tube, but the Prussic acid gas was unaltered.

R. *Experiment 11.* 0.5 of a cubic inch of sulphuretted hydrogen gas, the same volume of Prussic acid gas, and 0.25 of a cubic inch of oxygen gas, were attempted to be exploded by the electric spark, but they did not form an explosive mixture in these proportions, I therefore added 0.125 of a cubic inch more of oxygen, and again passed the electric spark through them, an explosion now took place attended with a diminution of volume amounting to 0.5 of a cubic inch; no red tinging acid was contained in the product of this experiment.

S. *Experiments 12, and 13.* Hydrosulphuret of ammonia added to simple prussiate of ammonia, and to prussiate of mercury, did not occasion the formation of any of the red tinging acid.

T. *Experiments 14, 15, and 16.* Sulphuret of carbon added to the two prussiates just mentioned, and also to liquid Prussic acid, was equally ineffectual as the hydrosulphuret.

U. *Experiments 17, 18, 19, and 20.* Sulphur was added to the same three liquids as the sulphuret of carbon, some sulphur was also kept in fusion while Prussic acid gas was passed through it, in neither of these cases was any chemical change effected.

V. *Experiments 21, 22, and 23.* Hydroguretted sulphur was added to the same three liquids with no better success.

W. *Experiments 24, 25, and 26.* Sulphur added to a strong solution of pure potash in the cold, so that no hydroguretted sulphur could be formed, was very sparingly dissolved in the alkali, the solution, or rather mixture of the two, was poured into each of the three liquids before mentioned, it did not alter the acid contained in them.

X. *Experiments* 27, 28, and 29. Sulphuretted sulphite of potash, prepared by adding sulphuret of potash to strong sulphurous acid, was employed in the same manner, but like all the preceding substances, it was found to be incapable of forming an atom of the red tinging acid.

The preceding series of experiments comprises all that I have made with the view of forming the red tinging acid ; they appear to prove,

1st. That this acid cannot be formed without sulphur. GH IKL.

2d. That it cannot be formed with sulphur, unless that substance be in the state of hydroguretted sulphur. MNOPQRS TUWX.

3d. That it cannot be formed with hydroguretted sulphur, without the presence also of an alkali. V.

It will be seen by reference to the successful experiments, that in them these essential conditions were fulfilled ; hence the indispensable agents in producing that peculiar change on the Prussic acid which constitutes it the red tinging acid, may be considered as determined ; the nature of the change which they effect will be best understood, after relating my analytical experiments on the red tinging acid, previous to doing which, I have to describe my process for obtaining the acid in a pure state from the liquid in which it is formed ; this process is the same in whatever mode the liquid has been obtained, it is the following :

Let the clear liquor be brought to a decidedly acid state by the addition of sulphuric acid, then keep it for a short time at nearly the boiling point, when cold, throw into it a little native black oxide of manganese finely pulverised, which will turn it of a beautiful crimson colour, filter this crimson fluid, and add to

it a solution containing sulphate of copper and green sulphate of iron, in the proportions of two of the former salt to three of the latter, until the crimson colour disappears, when a copious white precipitate will be formed, which is an insoluble salt of copper composed of the protoxide of that metal combined with the red tinging acid. This salt must then be boiled with a solution of potash which takes from it its acid, leaving the oxide of copper as a bright yellow powder. The acid thus transferred to the potash may be obtained in a free state by mixing this combination with sulphuric acid, and distilling it. The red tinging acid comes over, as a liquid strongest towards the end of the process, it is not however yet quite pure, as it will be found to contain a little sulphur and sulphuric acid, the best mode of separating both of which, is to add carbonate of barytes until the acid is saturated with it, and afterwards to throw down the barytes by the careful addition of sulphuric acid. The red tinging acid will thus be obtained in a state of perfect purity. In this state it is generally colourless, but sometimes acquires a pinkish hue, which I believe to be owing to a commencement of oxidation. In the most concentrated form in which I have obtained it, it had the specific gravity of 1.022, and a smell as pungent, and a little resembling that of strong acetic acid; at the boiling temperature it had a slight solvent action on sulphur, when the latter had been presented to it in a very divided state, but most of the sulphur thus dissolved separated again on cooling, the rest which it still retained after cooling, and which is foreign to its composition, may be detected by nitrate of silver, or by nitrate of protoxide of mercury, which form with the red tinging acid in the pure state, precipitates which are white and continue so, but with the acid holding sulphur in

solution, these precipitates have rather a dark colour. I proceed now to relate my

*Analytical Experiments on the Red Tinging Acid.*

A. I find that whenever this acid is distilled, a portion of sulphur remains behind in the retort, and the acid that passes over into the receiver contains a little in solution, at the same time a portion of the acid disappears, so that it would be possible, by repeated distillations, to destroy the whole of it. The nature of the new product produced by this repeated distillation I have not investigated any farther than to ascertain that it did not contain any Prussic acid. The sulphur that was separated was not in the hydroguretted, but in the common state.

B. Some of the red tinging acid was added to nitrate of lead, and an excess of nitric acid was poured into it. No precipitate was formed in the cold, but when heat was applied, a considerable action took place, attended with the escape of nitrous gas, and a copious white precipitate appeared, which, upon examination, proved to be sulphate of lead.

C. Five grains of the white salt of copper before mentioned, prepared with the most scrupulous care, and which I knew by an analysis (to be presently mentioned) contained 1.84 grain of this acid in a dry state, were totally decomposed by nitric acid in which muriate of barytes had been previously dissolved: they afforded by this treatment a white powder, weighing after ignition 15.82 grains, which by the subsequent action of nitric acid were reduced to 8.86 grains, and were sulphate of barytes, which is equivalent to 1.20 grain of sulphur.

D. Some of the red tinging acid was heated upon native

carbonate of copper or malachite in powder: during the operation there was a constant escape of carbonic acid from the malachite, and of Prussic acid into which one part of the red tinging acid was converted, whilst another part formed the white powder containing the protoxide of copper: now as all the copper in this ore was in the state of per-oxide, it follows that part of this oxide must have relinquished oxygen to some principle contained in the red tinging acid; the principle thus oxidated was found to be sulphur, for after the experiment on testing the liquid for sulphuric acid, the presence of that acid was most unequivocally demonstrated.

E. Some of the red tinging acid was mixed with diluted muriatic acid and hyperoxymuriate of potash; a gentle heat was then applied until chemical action took place, when the heat was withdrawn and the action moderated by cooling; by this process sulphuric acid was formed in the liquid, and Prussic acid also, part of which escaped as gas, and the rest was readily discovered in the liquid by neutralizing it and adding a solution of iron, with which it formed Prussian blue.

F. The red tinging acid was electrified negatively in the Voltaic circuit, and connected by cotton threads with distilled water electrified positively. The result of this experiment was, that the acid was carried over to the positive side without decomposition, or any separation of sulphur.

G. The above experiment was repeated, adding to the acid in the negative cup potash, and pouring into it mercury, into which the copper wire dipped that communicated with the battery. The result was the same as in the last experiment; the acid was carried over to the positive pole unaltered, and neither the potash, the mercury, nor the copper wire had



combined with any sulphur. That sulphur existed in this acid, both before and after this experiment, was however proved, by heating it in a mixture of nitric acid with muriate of barytes, by which means sulphate of barytes was quickly formed and precipitated.

From these analytical experiments on the red tinging acid, it appears to me that the following inferences may be drawn,

1st. That this acid contains sulphur. ABCDEG.

2dly. That this sulphur constitutes two-thirds of the weight of the dry acid. C.

3dly. That it exists in it, not as a foreign body in solution, but as an element. FG.

4thly. That when the sulphur is acidified, the other constituents of this acid unite in the form of Prussic acid, and that therefore they consist of the same elements as that acid. DE.

The results of these analytical experiments shew clearly why, in the synthetical ones, the presence of sulphur for forming it from Prussic acid was indispensable; they do not however so obviously shew why, besides the sulphur, the presence of both hydrogen and an alkali are requisite; probably the use of the hydrogen is to bring a sufficient quantity of sulphur into a state in which it is soluble in the alkali, while that of the alkali, by virtue of the mysterious power often termed disposing affinity, favours the formation of the stronger or red tinging acid, in consequence of its having a greater attraction for it than for the weaker Prussic.

I shall now drop the term red tinging acid, used merely in relating these experiments to avoid anticipating its nature, and having, as I think, proved that this acid is composed of sulphur and of the same elements as the Prussic acid, and that

consequently it belongs to the same class of acids as does the ferruretted chyazic acid, I shall call it henceforth the sulphuretted chyazic acid, and conclude this communication with giving some description of its salts, with my analyses of two of the most important of them, and by which the composition of all its other salts may be known with comparatively little trouble.

*Sulphuretted Chyazates.*

Of potash, a deliquescent salt soluble in alcohol.

Of soda, ditto, crystallizes in rhombs.

Of lime, ditto, soluble in alcohol, from which it may be obtained as a mass of needle form crystals.

Of ammonia, ditto, not crystallizable.

Of magnesia, ditto, when dried has a micaceous appearance.

Of alumina, crystallizes in octohedra which do not deliquesce.

Of barytes, a deliquescent salt, crystallizing in long slender prisms of a brilliant white colour.

Of strontia, a deliquescent salt crystallizing in long slender prisms in groups radiating like zeolite.

Of oxide of silver, a white insoluble powder.

Of protoxide of mercury, a white insoluble powder.

Of potash and prussiate of mercury, this salt is remarkable for its brilliant silvery lustre, and for its very compound nature, as all the four principles mentioned in the name which I here give it, enter into its composition. It has but little solubility in cold water, but is very soluble in hot, from which it may be obtained in crystals by cooling.

Of protoxide of copper, a white powder insoluble in water and in most acids, decomposable by alkalies or by distillation

with muriate of ammonia, also by mixture with nitrate of peroxide of iron; when mixed with five times its weight of hyperoxymuriate of potash it explodes, either by heat, friction, the contact of sulphuric acid, or by the electric spark. This explosion is very loud if it take place in a confined space, as in tubes.

Of per-oxide of copper, is best formed by adding sulphuretted chyzate of soda to sulphate of copper, both in a pure state; it is then in the state of a bright pea-green liquid, to which if any deoxidating substance be added, such as sulphurous acid, an alkaline sulphite, or the salts of protoxide of tin or of iron, then the sulphuretted chyzate of protoxide of copper is immediately produced, and precipitates in its usual form as a white powder.

Of protoxide of lead, a soluble salt, the forms of whose crystals, I am inclined to believe, are obtuse rhombs; in a moist atmosphere these crystals slowly deliquesce.

Sulphuretted chyzate of protoxide of iron, a colourless salt, very soluble.

Sulphuretted chyzate of per-oxide of iron, a salt of a beautiful crimson colour, deliquescent, and not obtainable in a solid form without great precautions, and a particular process, which consists in exposing it to an atmosphere artificially dried.

The sulphuretted chyzates of the following metallic oxides appear, by my experiments, to be all very soluble, viz. oxides of tin, bismuth, manganese, zinc, cobalt, nickel, palladium, uranium, molybdenum, and chromium.

The two sulphuretted chyzates that I have analysed are, that of protoxide of copper, and that of barytes.

*Analysis of sulphuretted Chyazate of Protoxide of Copper.*

A. Twenty grains of sulphuretted chyazate of protoxide of copper were heated to  $413^{\circ}$  for half an hour, without experiencing the least diminution of weight; consequently this salt does not contain any water.

B. Ten grains of crystallized sulphate of copper were dissolved in water, together with fifteen grains of green sulphate of iron, and were decomposed by sulphuretted chyazate of magnesia; the product was sulphuretted chyazate of protoxide of copper: after washing and drying at  $212^{\circ}$ , it weighed 4.58 grains. Now as the whole of the copper contained in the ten grains of sulphate entered into the composition of the 4.58 grains of sulphuretted chyazate in the state of protoxide, and as the quantity in those ten grains is according to PROUST 2.56 grains, which reckoned as protoxide is equal to 2.88 grains, it follows that 4.58 grains of the sulphuretted chyazate contain 2.88 grains of protoxide of copper, or 62.85 per cent.

C. Five grains of sulphuretted chyazate of protoxide of copper were decomposed by nitric acid, and the resulting nitrate of copper converted into a muriate, from which the copper was thrown down in the metallic state by iron; it weighed 2.82 grains, which reckoned as protoxide is equal to 3.172 grains, or to 63.44 per cent.

As this salt does not contain any water (A), its only constituents are sulphuretted chyazic acid and protoxide of copper, which exist in it in the following proportions.

	Experiment B.	Experiment C.	Mean of both.
Sulphuretted chyazic acid	37.15	36.56	36.855
Protoxide of copper	62.85	63.44	63.145
	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.000
	<hr/>	<hr/>	<hr/>

*Analysis of sulphuretted Chyazate of Barytes.*

A. Ten grains of this salt that had been previously dried at 212° and weighed immediately, were heated to 400° for half an hour without losing any weight.

B. Another ten grains in the same state of dryness, dissolved in water and decomposed by sulphuric acid, gave of ignited sulphate of barytes 10.5 grains, which contain according to BERZELIUS 6.93 of barytes.

C. Another ten grains in the same state, and also dissolved in water, were decomposed by muriate of protoxide of copper; they produced eight grains of sulphuretted chyazate of protoxide of copper, the acid contained in which, by my analysis of that salt, is 2.95 grains.

The sulphuretted chyazate of barytes fully dried at 212° is therefore composed as follows.

	Experiment B.	Experiment C.	Mean of both.
Sulphuretted chyazic acid	30.7	29.5	30.1
Barytes - - -	69.3	70.5	69.9
	<hr/>	<hr/>	<hr/>
	100.0	100.0	100.0
	<hr/>	<hr/>	<hr/>

The soluble sulphuretted chyazates are excellent tests not only for indicating the presence of oxide of copper in a solution, but also for shewing its quantity with great exactness, as

they precipitate the last atom of that oxide from its solutions in the state of an insoluble salt, whose composition is known. In order that it should have this effect however, the oxide of copper should exist in the solution as protoxide, (in which state it is seldom obtained in analyses) or which answers the same purpose, a deoxidating agent, such as sulphurous acid, or its salts, or a salt of protoxide of tin, or of iron, must be added to it.

Other useful applications of these salts and of their acid will also naturally occur to the ingenious analyst who wishes to avail himself of its peculiar actions on metallic bodies. It would be tedious to point these out, and their recital would extend a communication that is already of greater length than I could have wished, and which I here close.

Tower, June 6, 1814.