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IV. *An Analysis of the Waters of two Mineral Springs at Lemington Priors, near Wurtwick; including Experiments tending to elucidate the Origin of the Muriatic Acid.* By WILLIAM LAMBE, M. A. late Fellow of St. John's College, Cambridge. From the Memoirs of the Literary and Philosophical Society of Manchester, Vol. V. Part I.

[Concluded from p. 269.]

XI. FURTHER PROPERTIES OF THE OXYGENATED MURIAT OF IRON.

THE facts I have related are unquestionable: it was in the latter end of 1795 that I first made the observation on the effect of hepatised water upon iron: since then I have verified it repeatedly, and particularly in the month of December 1796, with some very pure iron, and in the presence of two gentlemen, very competent judges, one of whom assisted at every part of the process. Still it has been asked, How is it possible that this solution can contain muriatic acid, seeing that nitrat of silver, that most delicate test of this acid, is hardly affected by it? To this it might perhaps be a sufficient reply, that it is unreasonable to oppose a mere analogy to the direct evidence of the senses; particularly in a new case, where we have found some of the analogies best established in chemistry to fail. But let us recur once more to experiment.

I formed again some oxygenated muriat of iron. I suffered the acid to remain on the oxyde about 24 hours; then poured off the liquor, and evaporated the salt to dryness to expel the superfluous acid: the salt, which deliquesces instantly on cooling, was redissolved in a little distilled water. 1. I tried the solution with the acetite of lead: not the smallest cloud was produced. 2. The solution was then tried with the nitrat of silver: a little white curdy matter was formed. 3. A tea-spoonful of the solution was diffused through two or three ounces of distilled water, and then tried with the nitrat of silver: a very slight cloud was formed, and a minute purple precipitate fell, but not till after some hours. The appearance

ance was not so strong, nor the precipitate so copious, as when nitrat of silver is dropped into ordinary rain water.— These experiments evince, that this salt either does not decompose the salts of lead and silver, or that the new compounds are soluble in water. The first is absolutely conclusive: as to the small appearance of decomposition in Exp. 2 and 3, be it considered how difficult it is to prevent a minute quantity of common acid from passing over in the distillation of the oxygenated acid; and how readily this acid itself is decomposed: add to this the imperfect oxydation, perhaps, of the iron. If these circumstances are duly weighed, it seems probable, that this salt, when quite pure, would not at all sensibly decompose nitrat of silver. A slight impurity cannot be detected by acetite of lead, as a small quantity of muriat of lead is soluble in water.

XII. FURTHER CONSIDERATIONS ON THE HEPATISED SOLUTIONS.

Besides the oxygenated salts, I think it probable, that these solutions retain some sulphur; but under what form, or in what combination, it is not easy to say. The residuum, after evaporation, has a peculiar smell, whereas the pure salts are inodorous. The stain left upon silver by the residuum ought, perhaps, to be attributed to this cause. Also, the white matter formed by the decomposition of oxygenated muriat of mercury seems to be a combination of sulphur and mercury. In proof of this it may be remarked, that the precipitate of this salt dissolved in simple hepatised water is white. Further, it is doubtless true, that if hepatised water have a small quantity of acid mixed with it, the solution of iron strikes a purple colour with galls. To point out the origin of this colour, mix iron filings and sulphur not washed, and form them into a paste with a little water, and let them remain together for some hours: put the paste into water, and filtrate: this water now strikes a purple colour
with

with galls. Now, common fulphur is always contaminated with a little fulphuric acid; and, as neither hepatic gas nor oxygenated salt is here concerned, the effect must be attributed to the acid and the fulphur. If this water be evaporated, it leaves a matter which does not deliquesce; but which emits the same smell as the residuum of the hepatised solutions. To show that the acid is necessary to the production of the purple colour, let the fulphur be well washed with distilled water before it is mixed with the iron; and it will be found that no such colour can be now produced. The following fact seems to prove that fulphur may be retained in water, in the form neither of fulphur nor of hepatic gas: it is an additional proof how essentially the oxygenated differs from all the common salts of iron. I saturated a diluted solution of oxygenated muriat of iron, which scarcely affected nitrat of silver, with hepatic gas. A white precipitate fell, but so minute that it was impossible to collect it, nor did it destroy the transparency of the water: hence I think it probable that, if the salt were quite perfect, it would not be sensibly affected by hepatic gas. I now boiled the liquor, to expel the gas, till it wholly lost its hepatic smell. The liquor was again tried with nitrat of silver; and there was a copious deposition, but of a dark brownish colour. It seems certain, then, that some fulphur is retained by the solution, which cannot be expelled by boiling.

XIII. THE NEUTRAL SALTS OF THE WATER: MURIAT OF MAGNESIA, MURIAT OF SODA, SULPHAT OF SODA.

A gallon of the water was evaporated to dryness; the deliquescent salts were separated from the non-deliquescent; and each of the salts which were thus obtained was carefully examined. Thus, by processes which are sufficiently known, it was found that the gallon of water contains of muriat of magnesia 11.5 grains nearly; muriat of soda 430 grains; sulphat of soda 152 grains.

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The triple compound of which I have treated, is mixed with the deliquescent salt of magnesia, but not wholly; for it may be discovered with the non-deliquescent salts, though these have been separated carefully by spirit of wine. The tartrate of pot-ash indicates it in both. Oxalic acid does the same thing, separating a white powder with some crystalline grains which are the oxalat of manganese. (See Bergman, *Differt.* viii. 24.)

XIV. THE RESIDUUM OF DIFFICULT SOLUTION.

After these salts had been separated there remained a large residuum, which was not soluble except in a great quantity of water. This has a crystalline form like sulphat of lime; and of the usual reagents showed it, in fact, to contain both lime and sulphuric acid. But the weight of this residuum, from a gallon of water, was no less than 112 grains: a larger quantity than could be dissolved in a gallon of water, if it were pure sulphat of lime. If it be considered that the water requires some evaporation before these crystals begin to separate, the proportion is still more increased. There must be, therefore, something peculiar in the composition of the salt, or in the soluble powers of the water. Other experiments show the same thing. 1. Sulphuric acid dropped into the water precipitates copiously sulphat of lime. This cannot be effected by the decomposition of the muriat of lime: since we have already seen that no such salt is to be found (XIII). Indeed it cannot exist in the same solution with sulphat of soda, as these salts decompose each other*. 2. Sometimes a more unexpected appearance than this

* It is astonishing that this fact should have been neglected. and that in recent publications. Mr. Schmeisser, in his analysis of the waters of Kilburn Wells (*Phil. Transac.*), has joined together sulphat of soda, sulphat of magnesia, and muriat of lime, as being contained in these waters. Dr. Garnett has also put into the composition of the sulphur well at Harrogate sulphat of magnesia and muriat of lime; an error the more unaccountable, as Bergman has expressly remarked this decomposition in his *Dissertation on the Analysis of Waters.* See *Dissert.* ii. 7. M.

takes place. It is, that a precipitate, seemingly like the former, has been made by the addition of the muriatic acid : but by the addition of more acid the precipitate is redissolved. Sometimes, indeed most commonly, I have not been able to effect this appearance.

It was natural to expect the solution of any further uncommon observation in the same matter that had already explained so much. 3. I accordingly digested sulphat of lime in the hepatized solutions of iron and manganese ; and I found that the latter had a very strong solvent power. After the liquor had been filtered, sulphat of lime was plentifully precipitated by sulphuric acid. The solution of iron seems to have something of a similar property ; but as it is very small, and as iron has almost always a little manganese united with it, it is at least uncertain whether the whole effect ought not to be attributed to manganese.

It remains to compare this remark with the effects of the artificial oxygenated salts ; and thus to confirm, if confirmation were needed, the analogy which I have laboured to establish. 4. Sulphat of lime was digested with the oxygenated muriat of manganese and distilled water by a gentle heat : after 24 hours the clear liquor was separated : into this I dropped a little sulphuric acid ; by degrees a large quantity of sulphat of lime was separated. Muriatic acid was dropped into the same liquor, but it did not separate any thing. The oxygenated muriat of iron possessed the same property, but in so small a degree, that here again I am inclined to attribute this power to a little manganese attached to the iron. It follows from these facts, that the large quantity of sulphat of lime is kept in solution by the salt of manganese. And a further examination of the residuum itself shows that it contains the triple salt of manganese and iron. 5. Some of the residuum was perfectly edulcorated, and sulphuric acid was dropped upon it ; the vapours of muriatic acid arose, and were rendered evident by paper moistened with ammoniac or with simple water. To the sulphuric acid,

acid, which was used in this experiment, was added some distilled water, and the liquor was filtrated: it was then saturated with an alkali; a small precipitate fell, which was proved (by the usual methods) to contain both manganese and iron.

6. I have noticed a variation (2.) in the effect of muriatic acid when added to the water. I have observed a similar variety in the residuum itself; which is, that sometimes it has been found soluble in the muriatic acid: when this happens, the addition of an alkali precipitates the residuum in its original crystalline form; and this it does before the acid is saturated. But most commonly the muriatic acid does not dissolve it at all. Further, it has been said above (VII. 1.) that the acids precipitate a crystalline substance from oxygenated muriat of iron. This substance I have found to contain manganese. But what belongs to this place to observe is, that it is not always, indeed it is but rarely, that this effect can be produced in any great degree: in a very small degree it may always be observed; but, when I first remarked it, the precipitate was very copious, so that enough was readily collected for examination by the blow-pipe. The salt of manganese does not show this appearance in the smallest degree. It depends, therefore, on some peculiarity of the iron rust, but precisely on what I cannot take upon me to determine.

As the oxygenated salts unite with all the other salts of the water, and consequently cannot be separated by spirit of wine, I have found it impossible to determine the quantity of them.

I had concluded from the experiment (1.) that this water contained muriat of lime; and the following remark confirmed me in my error: I mention it, as I think it probable that others have been led into mistakes from the same cause. I reduced some of the water, by evaporation, to about two ounce-measures; taking for granted that by this process

nearly the whole of the fulphat of lime was separated. By adding sulphuric acid to this liquor, 20 grains of fulphat of lime were precipitated. I concluded, therefore, that this must have proceeded from the decomposition of muriat of lime: in truth, this fulphat was dissolved in the two ounce-measures of water, and was separated by the decomposition of the oxygenated salt.

ON THE WATER OF THE OLD BATHS.

THE spring which supplies these baths was discovered in 1786, in which year a cold and a warm bath were constructed. Upon sinking the well, a rock was found at the depth of eighteen feet; and the water rises from about the depth of three feet within the rock.

XV. THE GASEOUS FLUIDS.

I could obtain very little gas from this water, not more than three cubic inches from a gallon. It was azotic. An hepatic smell is perceptible when the water is fresh. To the hepatic gas, doubtless, it is owing, that no oxygen is found in this water or in that of the other spring. Dr. Garnett has so well explained the cause of this circumstance, that it is needless for me to enter upon it. (See Dr. G. on the Mineral Waters of Horrowgate, p. 74, &c.)

XVI. THE SPONTANEOUS PRECIPITATE.

This water is pellucid when it first rises from the spring; in small quantities it does not lose its transparency: a very small sediment is deposited by boiling, so small indeed that sufficient cannot be collected in this way for examination. However, when the bath has been newly filled, in some hours the transparency of this large body of water is destroyed by exposure to the atmosphere, and it contracts a whitish colour. I collected a large quantity of this precipitate from the bottom of the bath, where it by degrees accumulates. I first attempted its analysis by acids, but was disappointed. It is hardly soluble
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in any of the mineral acids : they all take up a little of it, make a brisk effervescence, and excite heat when first applied ; but neither by a long digestion, nor by boiling, could I saturate the acids ; nor, by putting a very small quantity of the powder into a large quantity of acid, could I completely dissolve the powder.

2. But by the use of the blow-pipe it readily appeared that this sediment is no other than the oxydes of the two metals so frequently mentioned, iron and manganese. It may be made magnetic ; it gives the hyacinthine colour to borax ; the colour is destroyed by continuing the fusion, and may be renewed by removing the globule to a silver spoon : fused with soda and nitre it makes a blue or a green globule. As the sediment may be procured in sufficient quantity, I repeated the last experiment on a larger scale : some nitre being mixed with it, the mass was pulverized, and fused in a crucible ; when taken out of the fire it was green, and dissolved in water, to which also it imparted a fine green colour : in a day or two a yellow ochre was deposited, when the solution became blue ; from this liquor a powder subsided by exposure to the air, which was manganese. (See Scheele's Essay on Mang. xxxvi. B.)

3. Pursuing the observations of the effects of the mineral acids confirms this conclusion. I mixed some of the sediment with powdered charcoal, and exposed the mixture to a strong red heat ; it became of a light brown colour, and now proved to be readily soluble in all the mineral acids. (See Scheele's Essay on Manganese, xxxviii. A.) With the muriatic and nitric it formed a gelatinous compound. The sulphuric acid, diluted, was soon saturated ; the liquor was evaporated, and deposited white crystals, the form of which is rhomboidal. This is a triple salt, the base of which is iron and manganese. If there be a small excess of acid, the taste is very like that of sulphat of argill. The same salt may be obtained by boiling the sulphuric acid with the sediment itself, and continuing the boiling till the mass is be-

come dry : the salt may then be procured by lixiviating the dry mafs, and cryftallizing the folution.

XVII.

Neither fulphat of argill nor oxygenated muriat of mercury is at all decomposed by this water.

XVIII. THE METALLIC SALTS.

All the appearances which demonftrate the exiftence of peculiar metallic falts in the waters of the new baths are alfo to be found in this ; as, the oxydation and folution of metals and a copious precipitate by galls, while the pruffiat of potafh is not affected (iv.) : and the fame experiments were repeated to fhew the prefence of the oxygenated falts of iron and manganefe (v. vii. &c.) with the fame refult, and authorize the fame conclufions. Still I believe there is fome difference in regard to thefe falts between the two waters. 1. I have already obferved (xvii.) two points of diftinction ; and, as the fecond of thofe experiments is probably an indication of fulphur, this water feems to be without it. This is confirmed by evaporating the water in a filver veffel, to which it communicates no ftain. However, 2. Its action on copper is very ftrong, fo that, if it be boiled in a copper veffel for a long time, a blue oxyd of copper is feparated from the veffel. But here, again, there is a difference between this and the former water ; for, though copper is diffolved in it, none can be precipitated on iron in its metallic form, as we have feen (iv. 1). The iron in this water does not feem to be in that high degree of oxygenation that it is in the other. This I infer, becaufe, 3. the precipitate formed by tincture of galls is of a much darker colour, even when the water has been much evaporated : fometimes, when the water has been reduced to half its original bulk, I have remarked even a very flight green tinge communicated by pruffiat of potafh, but not till it has been added to it many hours.

As the oxygenated salts are formed by the action of hepatic gas on the metals, it cannot be doubted that they are very common. Bergman (*Differt.* vii. 6.) observes, "that cold martial waters, when fresh, almost always have an hepatic smell:" it seems very probable then that this salt of iron may be found in almost all such waters. I doubt not that it has been frequently mistaken for muriat of lime, to which in its properties it approaches very nearly.

Though I have purposely avoided all medical discussion in this essay, I cannot abstain from bestowing a moment's consideration on one very obvious question. What, it will be asked, are the medical properties of manganese? Is it useful? Is it innocent? Is it noxious? That it is innocuous I certainly know. Dr. John Johnstone (*Essay on Mineral Poisons*, page 134.) has shown that it may be taken in large doses without injury; and he has informed me, that he has since confirmed the same fact frequently. I wish I could as well answer the first question; but what the medical virtues of this substance may be, is a subject which still remains in a great measure unexplored. It is certainly well worth the attention of men of science. To those who are inclined to labour in this field I take leave to suggest, that they should use either the carbonat or some other salt of manganese: the black oxyde, I apprehend, must be hardly soluble in the human fluids.

XIX. THE NEUTRAL SALTS.

These are the same as of the other water, but in different quantities. The gallon contains of muriat of magnesia 58; —muriat of soda 330; —sulphat of soda 62 grains.

XX. THE RESIDUUM.

A still larger residuum is obtained, after the separation of the neutral salts, from this than from the other water. The gallon leaves 146 grains. Its properties are the same as of that already described (xiv).

It is to be observed, that both these springs are affected by rainy weather; and that, consequently, their contents vary considerably according to the seasons.

SYNOPTICAL TABLE OF SUBSTANCES CONTAINED IN
THE TWO SPRINGS.

Gaseous fluids contained in a wine-gallon in cubic inches.

	WATER OF THE NEW BATH.	WATER OF THE OLD BATH.
Hepatic gas - - -	too small to be measured.	too small to be measured.
Azotic gas - - -	3.5	.3
Carbonic acid gas - -	.5	

Solid contents of a wine-gallon in grains.

Carbonat of iron - -	.75	
Oxids of iron and man- ganese - - -		too small to be weighed.
Oxygenated muriat of iron and manganese	unknown, but very small.	unknown, but very small.
Sulphur - - -	unknown, but very small.	
Muriat of magnesia -	11.5	58
Muriat of soda - -	430	330
Sulphat of soda - -	152	62
Sulphat of lime - -	112	146

Extract of a letter from Dr. HOLME, dated Sept. 25th, 1797.

“In the analysis of the waters of the new baths I have conjectured that the decomposition of oxygenated muriat of mercury is occasioned by a minute portion of sulphur, attached to some of the substances dissolved in the water (111.). I have attempted to verify this conjecture, and not without success. Wishing to collect some quantity of the precipitate, I evaporated a gallon of the water to half its bulk; but found, that now the salt of mercury was dissolved without decomposition. I added, therefore, the salt to the water without boiling; and suffered the precipitate to subside. By this process, I could collect no more than a grain from a gallon of water. I threw this upon alkali heated to redness; but
the

the whole instantly evaporated with a dense smoke. I mixed, therefore, another portion (procured in the same manner) with alkali, and heated them in a crucible: still I failed to collect any sulphur from the alkali (as I had hoped); but I now perceived that, as the crucible became hot, the matter burnt away with a blue flame, as sulphur does.

“Sulphat of argill is not decomposed by this water when it has been reduced by evaporation: however, it gradually separates some of the abundant sulphat of lime; which is probably caused by its attracting the water which held it in solution.

“I think it right here to observe, that I have recently met with this water in such a condition that it caused a permanent decomposition of sulphat of argill. This precipitate is extremely minute: I have not as yet determined the cause of it, but I suspect it to be carbonat of magnesia.”

V. *Second Memoir on the Metal contained in the Red Lead of Siberia.* By Cit. VAUQUELIN. *From the Annales de Chimie, Vol. XXV. 1798.*

I HAVE already shown in my first memoir on the red lead of Siberia, that this mineral contains a particular metal, which I promised to examine with more attention. The Council of Mines having furnished me with a pretty large quantity of the red lead, considering its scarcity, I have been able to make a series of experiments sufficient to determine its principal properties, of which I shall now give an account; but it will first be necessary to recapitulate, in a few words, the substance of my former memoir, in order that what I have to say at present may be rendered more intelligible.

1. I shall observe, that on boiling the red lead reduced to a powder with two parts of the carbonat of pot-ash, the lead

* See page 279.