XI. *Analysis of the Arseniates of Copper, and of Iron, described in the preceding Paper; likewise an Analysis of the red octaedral Copper Ore of Cornwall; with Remarks on some particular Modes of Analysis. By* Richard Chenevix, *Esq. M. R. I. A. Communicated by the Right Hon. Sir* Joseph Banks, *Bart. K. B. P. R. S.*

Read March 5, 1801.

SECTION I.

ARSENIATES OF COPPER.

THE endless diversity which the hand of Nature has diffused through all her works, even when she makes use of the same primitive materials, must sufficiently convince us, that, whatever accuracy we may attain in the knowledge of the latter, the means which she employs to form her combinations are still secret. The intellectual eye may indulge in the contemplation of hypothetic systems, which itself has created, and which it alone can behold; but, how far removed must they ever be from truths, evident to our senses, and supported by palpable experiments.

To follow Nature through the minutiæ of her labours, and behold her reproducing the same primitive materials in many different shapes, has always been deemed a less splendid achievement of science, than to discover one more of those simple substances, by the union of which she forms the complicated effects we daily admire. Yet to me it appears, that, in no instance is she more truly wonderful, than in the unbounded variety which she has sometimes produced from a small fund of original resources; and, when we can fairly follow a few primitive substances, through a series of combinations infinitely multiplied.

In addition to the two chymists who, as is mentioned in the preceding Paper by the Count de BOURNON, appear to have had some knowledge of the existence of a natural arseniate of copper, I must name M. VAUQUELIN. In a letter to me last year, he communicated the discovery of such a substance in France. Of the different varieties which these gentlemen, Messrs. KLAPROTH, PROUST, and VAUQUELIN, have examined, I shall have occasion to speak, in the course of these experiments: but it was reserved for the Count de BOURNON, to state, in the said Paper, with his usual talent and perspicuity, the scientific detail of the external characters, particularly of the crystalline forms, by which he had identified their nature. The free access to the extensive collections of the Right Hon. CHARLES GREVILLE, and of Sir JOHN ST. AUBYN, also the easy communication with the native soil of this mineral, were the peculiar advantages, which enabled the Count de BOURNON and myself to pursue the mineralogical and chymical researches, which are stated in these communications to the Society.

When the Count de BOURNON had completed what appeared to him to be the mineralogical classification of these copper ores, he gave me some specimens of each kind, numbered indiscriminately, for the very purpose of excluding prejudice; and it was not till my task was ended, that we compared our observations. If I had been admitted into any previous knowledge of the arrangement dictated to him by the principles of crystallography, I should have been afraid, that I had merely thought true, what I wished to be so. But I can, most conscientiously, indulge in the satisfaction which the according results of different means to prove the same proposition naturally excite; and which is justly due to the truth of the outward marks, however delicate, yet still to be perceived, that nature has left visible to those who will observe her.

I shall now proceed to offer the result of a chymical analysis, undertaken with a view to determine what confidence the crystallographical arrangement, adopted in the preceding Paper, might merit; and to shew how far sciences so nearly allied, may receive new light and confirmation from reciprocal aid.

I shall confine myself to detail only those general processes which, upon frequent trial, have been found preferable. By reducing to powder any of the arseniates of copper here spoken of, and then exposing them to heat in a platina crucible, the water of crystallization was quickly dissipated. But, as too great a degree of heat volatilized some portion of the arsenic * acid, it was found necessary to moderate the heat;

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* There is no doubt that philologists, who do not consider the principles of the new methodical nomenclature, may, at first sight, think the term *arsénic* objectionable; particularly as previous custom and analogy had given another denomination, *arsenical*, which is the natural adjective of the substantive *arsenic*. They may say, that the difference of accentuation alone marks the distinction between the substantive and the new adjective. But every chymist will set the weightier considerations of method and order before such objections. In French, the termination in *ic*, for

and, in order that every particle of water might be finally expelled, to prolong it. When the diminution of weight was ascertained, the residuum was dissolved in acetous, or, still better, in dilute nitric acid, and nitrate of lead was poured in. Arseniate of lead and nitrate of copper were thus formed, by double decomposition; but, when more nitric acid had been used than was strictly necessary to dissolve the arseniate of copper, no precipitate appeared, till the liquor had been evaporated. When the evaporation was pushed too far, part of the nitric acid, contained in the soluble nitrate of copper, flew off; and that nearly insoluble cupreous nitrate, first mentioned by Mr. PROUST,* was produced. To obviate both inconveniences, alcohol was added, immediately before the liquor was quite evaporated, and long after the precipitate had begun to appear; in a few minutes, all the arseniate of lead fell to the bottom, while the nitrate of copper was held in solution. These new products being separated by filtration, the spirituous liquor was distilled; and, from the nitrate of copper, the quantity of

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the substantive, and in *ique,* for the adjective, obviates all confusion. One remark I shall beg leave to offer to the consideration of those chymists, who have laboured to adapt to the English language, a literal translation of the French nomenclature. It is the genius of the former language, to throw the accent as far back as possible; so that, in trisyllabical nouns, the first or second syllable is usually accented; while, in the French language, the accent is generally thrown upon the last: thus, we say *sulphúric acid,* but they say, *acide sulphuríque.* It was very natural therefore, as in the latter case, to make the accented syllable be that, which should denote the particular state of the substance of which they speak. Thus *sulphuríque, sulphureúx*; *nitríque, nitreúx*; *sulpháte, sulphíte*; *nitráte, nitríte.* But, without offending the radical orthoepy of our language, we cannot make the same method subservient to that purpose; for, when we wish to mark the distinction in that manner, we are obliged to wrest the word from its proper pronunciation, and to say, *nitríc, nitróus, sulphureoús,* &c.

* Annales de Chimie, Vol. XXXII. p. 26.

that metal contained in the ore was obtained, by boiling the solution with pot-ash or soda.*

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* By potash and soda, I mean those alkalis pure, obtained according to the method prescribed by BERTHOLLET. I know of no other. It is not, that I have any predilection for those identical terms; yet, whatever melioration subsequent improvement may introduce in particular cases, if principles are to be adopted, they should, in general, be strictly adhered to. But it must be a violation of them, to apply a word, appropriated by common consent to design a pure, and as yet a simple substance, to such heterogeneous mixtures as lapis causticus, carbonates of potash and soda, &c. It is indeed much to be desired, that the epithets, *caustic*, *pure*, *saturate*, &c. should be regarded as tautology, which they really are. There is no potash purer than potash. When it is not pure, we should say, instead of "I took so much potash," "I took so much of a mixture of potash, and, whatever other substance is mixed with it." Thus, instead of calling lapis causticus, caustic potash, or potash, as is often done, we should say, "I took so much of a mixture of potash, sulphate, muriate, carbonate, and sulphuret of potash; siliceous and aluminous earths; iron and manganese;" for such I find, by analysis, lapis causticus to be. To all this is added, by apothecaries, a little lime. Yet this is the substance sometimes called potash.

M. LOWITZ's manner does not give potash pure enough for delicate analyses of stones. I have never seen any prepared by his method, in which I could not discover iron, silica, alumina, and carbonic acid. To the proofs given by Dr. KENNEDY, (in his paper entituled "A Chymical Analysis of three Species of Whinstone, and two of Lava, in the Edinburgh Transactions for 1799,) of the efficacy of his method, I propose the following objections. That chymist supersaturates by nitric acid, and examines by nitrates of barytes and of silver. This will be a sufficient test for sulphuric and muriatic acids; but carbonic acid may have been present before saturation. He then evaporates; and, if all is redissolvable, concludes there is no silica or alumina; but, after saturation by an acid, ammonia is a more delicate test than evaporation, for small portions of those earths.

By treating Dantzic potash, or, still better, pearlash, with lime, and evaporating in a well-plated copper vessel, a white mass is left. This mass, dissolved as far as it can be in alcohol, and the liquor distilled to dryness in a plated alembic, gives an alkali of a perfect whiteness. In this state, it is dangerous to touch it; its action on animal matter is so sudden, and so violent. It attacks all stones with the greatest ease and rapidity. Dissolved in water, it makes not the least cloud in barytes water, or in a solution of nitrate or muriate of that earth; and may be used, as a very delicate and sensible reagent, to distinguish it from strontian. By saturating with an acid, and then

To the use of alcohol, in order to get rid of the excess of acid, as mentioned above, there is not the same objection that there might be to evaporation, or to an alkali: it can combine with that acid only which is free; and an excess of it can, in no way, affect the metallic salts.

I have given the preference to lead, above every other method of combining arsenic, to determine its quantity in any other body, having found arseniate of lime, which has been hitherto recommended, as well as all other earthy arseniates, to be nearly as soluble in water as sulphate of lime. Lead presented also much facility as to the proportions of its arseniates; and a few experiments, instituted to arrive at them, afforded sufficient accuracy. But, first, it was necessary to ascertain how much acid a given quantity of metallic arsenic could afford; and, finding that it was in vain to aspire at a greater degree of precision, than that which Mr. PROUST had obtained, I have adopted his results. By them it appears, that 133 of white oxide, and 153 of acid, contain each 100 of real arsenic, the rest being oxygen. But, 100 of metallic arsenic, acidified by nitric acid, neutralized by an alkali, and precipitated by nitrate of lead, gave 463 of arseniate of lead; that is, 100 of arseniate of lead, contain 33 and a fraction of arsenic acid; and, on the other hand, my own experiments informed me, that lead, dissolved in nitric acid, and precipitated by arseniate of ammonia,

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seeking silica, or alumina, by ammonia, no trace of them can be found, nor indeed of any thing else. I do not say, however, that the potash is perfectly free from every other substance; I believe it contains a little carbone, produced by the decomposition of the alcohol, and is, therefore, a subcarburet of potash; but carbone can be of no consequence, in the generality of experiments, in humid docimasia. The same method, employed with carbonate of soda, is the only one to procure soda in a state of equal purity.

gave a proportion of 63; and 4 were expelled by heat from this salt. The composition of arseniate of lead, therefore, is,

Arsenic acid - - - -	33
Oxide of lead - - - -	63
Water - - - -	4
	100

This experiment, repeated several times, never gave 1 per cent. difference in the results. Another method, which may be deemed shorter, and perhaps even more accurate, to analyze arseniate of copper, is as follows. After the quantity of water has been estimated, the remainder may be treated by either of the fixed alkalis, which will combine with the acid, and leave the brown, the only real, oxide of copper, in the same state as that in which it existed in the ore; the alkaline liquor may be neutralized, as above, and the proportions determined in the same manner.

No. I. *Third species of the preceding Paper.* One hundred parts, exposed to a low red heat, lost nothing of their weight. Dissolved in dilute nitric acid, decomposed by nitrate of lead, and precipitated by evaporation, and then by alcohol, they left a white powder, which, well washed and dried, weighed 121. But 121 of arseniate of lead, contain 39,7 of arsenic acid. The nitrate of copper, boiled with potash, left a precipitate, which weighed 60. Therefore, there are in this variety,

Oxide of copper - - - -	60
Arsenic acid - - - - -	39,7
	99,7

No. II. *Fourth species of the preceding Paper.* One hundred parts, exposed to a low red heat, lost 16. Treated as above, they yielded a quantity of arseniate of lead, corresponding to 30 of arsenic acid; and I obtained 54 of oxide of copper. Therefore, this variety contains,

Oxide of copper - - - -	54
Arsenic acid - - - - - -	30
Water - - - - - - - -	16
	100

No. III. *Var.* 2 *of the third species.* One hundred parts, exposed to a low red heat, lost 18 of water. The 82 remaining, boiled with potash, left a residuum of a blackish brown colour, which weighed 51, and which, examined by the different reagents, was found to be oxide of copper, without mixture. The supernatant liquor, and the liquor which washed the 51 precipitated, being neutralized and evaporated together, left a precipitate, by nitrate of lead, which weighed 88, and, by the proportions of arseniate of lead, established above, indicated 29 of arsenic acid. The proportions in this variety are therefore as follows:

Oxide of copper - - - -	51
Arsenic acid - - - - - -	29
Water - - - - - - -	18
	98

No. IV. *Var.* 5 *of the third species.* This gave, by one or other of the two methods, already described and applied, as follows:

Oxide of copper - - - -	50
Arsenic acid - - - - - -	29
Water - - - - - - - - -	21
	100

No. V. *Second species of the preceding Paper.* This is the variety which, according to the description I received from M. Vauquelin, he had analyzed. In his letter to me, he gave no particulars of the method he had employed, but merely stated his result.* By that, it appears to contain,

Oxide of copper - - - -	59
Arsenic acid - - - - -	41
	100

Before the reception of his account, I had found,

Oxide of copper - - - -	58
Arsenic acid - - - - -	21
Water - - - - - - -	21
	100

This induced me to repeat the analysis with the greatest care and attention; for I thought, that to differ from so great a master must be to differ from truth; but I constantly found 21 of water, and 21 of arsenic acid.

This apparent difference must, therefore, depend on the state of dryness in which he obtained his acid; or perhaps he estimated it with the water; and, if so, I am happy to find I agree with him so near as one per cent. A greater precision, as every person familiar with analysis well knows, is not within the power of chymical exactness.

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* J'ai analyzé, ces jours derniers, une mine de cuivre d'un vert clair cristallin, en lames hexaëdres, se divisant en lames menus, et legèrement flexibles, comme le mica; et c'est pour cela, que les naturalistes l'avoient nommé *mica vert.* J'ai trouvé que ce mineral étoit composé d'environ 59 d'oxide de cuivre, et de 41 d'acide arsenique; et c'est de véritable arseniate de cuivre. Paris, August 30, 1798.

No. VI. *First species of the preceding Paper.* One hundred parts, exposed to a low red heat, lost much more than any of the other kinds; the deficit amounted to 35. The usual treatment gave 49 of oxide of copper, and only 14 of arsenic acid. I repeated this analysis, with some portions which had not been exposed to heat, and never found more than 14 of arsenic acid. This arseniate contains,

Oxide of copper - - - -	49
Arsenic acid - - - - - -	14
Water - - - - - - - -	35
	98

No. VII. *Yellow hematitic copper ore.** (See page 171.)

One hundred parts of this ore, boiled with dilute nitric acid, left a yellowish white residuum, which weighed 17. These 17, exposed to a degree of heat sufficient to volatilize the sulphur, left 5, which were silica. The liquor from which this residuum had been separated by filtration, upon being tried for all the different metals, and particularly for arsenic, afforded no traces of any thing but copper and iron. A copious precipitate took place by the affusion of ammonia; the copper was redissolved by adding an excess; and then obtained by volatilizing that alkali, and boiling with potash, after the filter had separated the iron already precipitated. The contents are,

Sulphur - - - - - - - -	12
Silica - - - - - - - -	5
Copper, which I believe to be in the metallic state	30
Oxide of iron - - - -	53
	100

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* This and the following (No. VIII.) being the matrices upon which the arseniates of copper and of iron are generally found, I thought it right to give an analysis of them also.

In this ore, I believe, for the following reasons, that the metals are in the state I have marked. First, the proportions in the ore announce it; for I always had an excess of weight in the total result, if I did not deduct such a proportion of oxygen as might be contained in 30 parts of copper.

Secondly, there is a considerable disengagement of nitrous gas.

Thirdly, the ore does not attract the loadstone.

And, fourthly, the greater part of the iron, (but none of the copper,) is dissolved in muriatic acid, forming a green muriate of iron, without disengagement of hydrogen gas.

No. VIII. *Grey vitreous copper ore.* (See page 173.) There are many intermediate states between this ore and the yellow hematitic copper ore; but they are not fair objects of chymical analysis, being merely mixtures of both kinds, in different proportions. The mineralogist, indeed, may dwell upon them, as interesting in studying the products of nature, but they are unsatisfactory subjects for the chymist.

Grey vitreous copper ore, when obtained in its greatest purity, is by many degrees the richest cupreous pyrites known in nature; and, in the large way, the metal may be extracted by the easiest processes. 100 parts of this ore, in dilute nitric acid, left 12, which were sulphur. Ammonia, poured in excess into the nitric solution, redissolved, with the exception of 4, the whole of the precipitate which it had formed; the 4 were iron; and, from the ammoniacal liquor, 105 of black oxide of copper, equal to 84 of metallic copper, were obtained by evaporation, and then boiling with potash.

Sulphur - - - - - -	12
Copper - - - - - -	84
Iron - - - - - -	4
	100

Although I have mentioned, in the preceding statements, only a single analysis of each specimen, it is by no means to be imagined, that so small a number would be sufficient to satisfy enquiry. None of the above results have been taken into account, unless confirmed by frequent repetition ; and the probationary experiments have been diversified, as much as lay in my power, by many different tests, and various chymical reagents.

With regard to the colour of some specimens of arseniate of copper, it is easily to be accounted for upon chymical principles. The mistake under which we have long laboured, that the green is the real oxide of copper, has happily been rectified by M. PROUST.* He has proved it to be a particular substance, (to which he has given the very improper name of hydrate of copper,†) endowed with peculiar properties, and composed of the brown oxide, and of water, in a state of combination. From his experiments, and from what I myself have seen, I am inclined to draw the conclusion, that we have never yet obtained by art any real salt of oxide of copper. In examining, for instance, sulphate of copper, we find it to afford blue crystals; and to

* Annales de Chimie, Vol. XXXII. p. 26.

† Copper is not the only metal capable of a similar combination. Cobalt, nickel, and uranium, enjoy the same property. This may, in some measure, explain the change of colour, which the liquid muriates of some of these metals undergo by gentle heat: it may likewise throw some light upon the sympathetic ink of Cobalt.

contain a known quantity of water of crystallization, and of what we formerly called the oxide. But that oxide still retains a quantity of water, of which when it is deprived, it passes to a very dark brown, and changes its chymical nature and properties.

If, upon that brown oxide, a sufficient quantity of dilute sulphuric acid is poured, it yields a blue salt, but in a proportion greater, by about 24 per cent. than if the green substance had been employed. I imagine, therefore, that the first operation of this brown oxide is, to assume the quantity of water necessary to constitute a hydrate; and, that the combination of sulphuric acid takes place, not between the oxide, but between the hydrate and that acid, to form a salt, which, when crystallized, has taken another portion of water in the act of crystallization. It is a well known fact, that there is a state of concentration, when an aqueous solution of muriate of copper, gently heated, will change from a bluish green to a beautiful brown, which, upon cooling, or by the affusion of water, resumes its former tinge. This brown liquor is probably a solution of muriate of copper; while the blue liquor, like every green or blue solution of a cupreous salt, is a combination of the acid and the hydrate, or (as we should say in this case) a muriate of hydrate of copper. It is true, I have not been able to produce, so often as I could wish, this change of colour. I can, however, adduce the following instance, as being much in favour of my opinion.

It is evident that oxide of copper (for so I shall henceforth call the brown substance) has a very strong affinity for water; because the fixed alkalis, (unless when boiled upon it,) and their carbonates, all of which easily decompose the salts of copper, cannot dispossess the hydrate of copper of its water.

This led me to imagine that I could perhaps, by fire, dissipate not only the water of crystallization, but that contained in the hydrate; and leave the acid, if a potent one, still in the salt. But I found that the affinity of the alkali, acting upon the acid, had, in the humid way, determined an order of combination not to be effected by heat; for, even sulphuric acid was expelled, before the water of the hydrate could be completely dissipated. Upon reflecting on the fixity of acids, I could find none so proper for this experiment as the phosphoric. I therefore prepared some artificial phosphate of copper, by precipitating the nitrate of that metal by phosphate of soda. When washed and dried, it was in the form of a fine bluish green powder, among which, many crystals were discernible, almost to the naked eye.

One hundred parts of this, exposed to a gentle red heat, became of a much paler green, but passed intirely to brown when the temperature was sufficiently elevated. I had then a brown phosphate, not of hydrate, but of oxide of copper, and from which no acid had been volatilized. Its loss of weight was wholly from the water which had been expelled, and amounted to 15,5. Its other proportions I found, by further analysis, to be 35 of phosphoric acid, and 49,5 of oxide of copper. It is not, however, to be concluded from this, that there are really 15,5 of water of crystallization, in bluish green phosphate of copper. We must recollect, that it is a phosphate of hydrate of copper; and that 49,5 of oxide demand 12 of water, to exist in that state: 3,5 therefore are the amount of the water of crystallization; and its order of union may, with more propriety, be thus stated:

Oxide of copper	49,5	forming hydrate of copper	61,5
Water	12		
Phosphoric acid			35
Water of crystallization			3,5
			100,0

And this is the order which should be adopted, in the statement of all analyses of salts of copper.

I could easily produce, by the same method, a pale green, or a brown arseniate; and, in nature also, the colour of the ore accurately corresponds with the proportion of water, as may be seen by comparing together any of the foregoing analyses.

Having thus convinced myself, by analysis, that copper is found in nature united with arsenic acid in different proportions, I next wished to ascertain, whether art could effect similar combinations. For this purpose, I poured into arseniate of ammonia, a solution of nitrate of copper. The metallic arseniate was immediately precipitated in crystalline grains, of a blue colour, rather more intense than the phosphate already mentioned; and the liquor, which remained blue, was decanted. The colour which this latter retained, I imagined, was due to the presence of a greater quantity of nitrate of copper than was necessary to precipitate, from its alkaline basis, the arsenic acid combined with the copper. After a partial evaporation, I poured in alcohol; and found, to my surprise, that the consequence was another precipitation, which was much increased by allowing the liquor to remain. Crystals, still more rich in colour than the former, and very evidently rhomboidal, even to the naked eye, were gradually formed. Imagining there must be some essential cause of the greater solubility of the one than of the other, I resolved to examine them apart.

One hundred parts of the first of those precipitates, exposed to a low red heat, lost 22. Boiled with potash, there remained undissolved, a blackish brown powder, which, well washed and dried, weighed 50. The supernatant liquor, saturated with nitric acid, and evaporated, was precipitated by nitrate of lead. Upon filtration, 82 were left, which indicate 27 of arsenic acid. Therefore, this arseniate of copper contained,

Copper - - - - -	50
Arsenic acid - - - -	27
Water - - - - -	22
	99

The second artificial compound, which was mentioned above, was evidently more soluble than the latter; and analogy might lead us to suspect, in arguing from the generality of salts the basis of which is supersaturated, that it contained an excess of acid. It was analyzed in the same manner as the last, and afforded,

Oxide of copper - - -	35
Arsenic acid - - - -	39,5
Water - - - - -	24
	98,5

Thus then have we two artificial arseniates of copper, one of which intimately corresponds with one of those which we have recognized among the productions of nature. The other possibly will be found, but we are not yet in possession of it; for I shall presently mention the reason why No. I. although containing 39 of acid, cannot fairly be esteemed as such. I have not yet been so fortunate as to form the other combinations; but do not doubt, that art may one day succeed in obtaining them.

REMARKS.

Before I conclude this section, which hitherto has had for its object a particular account of certain kinds of copper ore, as well as of their matrices, it may not be superfluous to offer a few remarks, not foreign to the present subject, upon some methods generally used in the docimastic art. To prove the presence of different substances in fossils, is an object of delicate research; but, to determine proportions with accuracy is the most difficult operation of analytic chymistry, and often eludes investigation. It is rather a pleasing reflection to think, that we are in the infancy of chymical exactness; and that we may see the day of improvement, when the errors which we now commit will require all the aid of self-complacency to be in the least excused. And it may be of more real utility to state with frankness, although we cannot account for them, those anomalous appearances which so frequently occur, than to court the phantom of rigid accuracy, the reality of which we can as yet, but in a few instances, be sure we have attained. For, every observation, however trivial, of this kind, will hasten the arrival of that moment when we shall be enabled to approach a little nearer to truth.

I have, for many reasons, preferred boiling the nitrate of copper with either of the fixed alkalis, to the method generally recommended, which is, to precipitate all the copper from its solvent, by carbonate of potash, or of soda; then, to redissolve in muriatic acid; and to precipitate, in the metallic state, by a plate of polished iron.

First, when an alkaline carbonate is used, the precipitate is a carbonate of hydrate of copper; and this substance is soluble in an excess of the precipitant. I once evaporated some very beautiful blue liquor, obtained in an operation of this kind, and found a crystallized salt, which I became desirous to examine. But, as the solution contained another salt, formed by the acid (which originally held the copper in solution) and the alkali employed, I found it necessary to form some hydrate of copper directly for the purpose.

Some hydrate of copper was therefore prepared, by decomposing the nitrate of that metal by a very dilute solution of potash, and well washing and drying the precipitate: it was that fine powder formerly well known as the oxide of copper. Some of this substance was thrown into a solution of carbonate of potash, through which a current of carbonic acid had been made to pass for a long time, and they were then slightly heated together. One part of the hydrate became of the same colour as the real oxide; the other was dissolved, and the liquor was converted into a greenish blue solution. Thus, one part of the hydrate had yielded its water to the other, in order to favour this quadruple, or rather this double combination, of carbonate of potash and hydrate of copper: the liquor, when reduced, afforded a mass, which, repeatedly redissolved and evaporated, with difficulty assumed any determinate form of crystallization. This salt is a carbonate of potash, holding a little copper. It is of a pale blue, and varies in colour, according to the quantity of water of crystallization, and of metal. It is slightly deliquescent, and soluble in about three parts of water, at 60°, but requires much less water, when the water is boiling. It crystallizes by cooling, much like carbonate of potash. It is soluble in a large quantity of alcohol. It loses about 43 per cent. of carbonic acid, by solution in a stronger acid; and, prepared in the manner I have mentioned, contains no more than 5 per cent. of oxide of copper; although carbonate of potash, when poured into a solution of any salt of copper, appears to retain a much greater quantity. This, therefore, is a sufficient proof of the inaccuracy of attempting to precipitate copper from its solutions, by an alkaline carbonate; for, carbonate of soda has, like carbonate of potash, the property of dissolving and crystallizing, as a triple salt, with hydrate of copper.

In addition to this source of error, we may add, the very uncertain operation of one metal upon the saline combination of another, whatever may be their affinity for oxygen. Indeed I have so often remarked this very great uncertainty, that I was pleased to find the observation had occurred to Mr. PROUST; and I have constantly found that more dependence can be placed upon the method I have adopted, than upon any attempts to precipitate the metals by each other.

With regard to efficacy and promptness, tin or zinc is preferable to iron; but, with any of the three metals, a phenomenon occurs, for which I have not been able to account, in any manner the least satisfactory. As the effects are more striking with zinc than with the other metals, I shall enter into particulars respecting the use of that metal only.

When a bit of zinc (or tin, or iron,) is immersed in a solution of muriate of copper, a precipitation begins, and all the copper is finally separated in a few hours.* But, if a little muriatic acid is added to this solution, and the zinc then immersed, a violent

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* If any quantity of neutral salt is present in the solution, the precipitation is much retarded, and is seldom complete.

effervescence takes place; hydrogen gas is disengaged, and, in less than two minutes, the copper is so completely precipitated in the metallic state, that neither ammonia, nor even sulphurated hydrogen, can discover any vestige of its presence.

It would appear from this, that hydrogen is, in this case, the real reductive and precipitant of the copper. Yet, how can we reconcile the evident contradiction that, in one case, zinc with muriatic acid will decompose water, that is, that zinc and muriatic acid will attract oxygen more strongly than hydrogen can, yet that, in the other case, hydrogen, whose affinity for oxygen is weaker than that of zinc and muriatic acid, will be more speedy and powerful than zinc and muriatic acid, in attracting that oxygen from copper. Again, how is it possible that zinc and muriatic acid will, in preference to taking oxygen immediately from the oxide of copper, decompose water, the hydrogen of which will unite with the oxygen of the oxide of copper, again to become water, which it originally was. All this appears to me, I confess, as contradictory as to say, one is less than two, two are less than three, yet three are much less than one. This opinion, that hydrogen is really the reductive, is the more extraordinary, as it is not founded on the single experiment above-mentioned.

If a bit of zinc (or tin, or iron,) is thrown into a solution of oxide of arsenic in water, no change of any kind will be effected, even after a considerable time. But, the instant that muriatic acid is added, effervescence and precipitation commence; a few minutes suffice to obtain all the arsenic in its metallic state. It may be objected here, that muriatic acid, (as muriatic acid,) produces some hitherto unknown modification in the order of established affinities. This objection is not plausible; and I can adduce so clear an answer to it, as to shew that it is of very little moment. If aqueous arsenic acid is used, instead of the above solution, the same phenomena of effervescence and precipitation ensue, as when muriatic acid had been used in the former case; and that precise quantity of metallic arsenic is thrown down, which can yield sufficient oxygen to the zinc to combine with the remaining acid undecomposed. The precipitate which is formed, is a mixture of metallic arsenic with arseniate of zinc; and these may be separated by muriatic acid, which will dissolve the metallic salt, without acting upon the arsenic.

If, instead of muriatic acid, sulphuric acid is used, the same phenomena take place, in a less degree. But, if the experiment is tried with nitric acid, there is no disengagement of hydrogen gas; and the metals effect a precipitation with much less rapidity and certainty than in the former case.

It is very true, that hydrogen, in its nascent state, may have properties with which we are yet unacquainted; and may determine combinations, which it can in no other state produce. But the decomposition of water, in the first instance, in order that a new recomposition may, at that moment, be effected by the same agents, is in itself sufficiently paradoxical.

The facts last mentioned, are somewhat analogous to, and seem even confirmative of, a theory proposed some time past by Mrs. FULHAME; but I shall withhold my full assent, both to her explanation and to any I could give, until these evident contradictions can in some way be further elucidated.

In the analysis of every ore in which the metal is combined with sulphur, I have found much variation in the quantity of the latter which may be obtained, even in experiments upon the same specimen. If nitric acid is used not sufficiently strong, part of the ore remains untouched, and will require subsequent treatment, always disadvantageous in delicate operations. If the acid is too strong, a great part of the sulphur is converted into sulphuric acid; so that, in either case, there is room for error. I thought that, to avoid this, (except in cases where any metal which, with sulphuric acid, forms an insoluble salt, was present,) strong nitric acid might be used, and all the sulphur converted into acid. If potash, soda,* or ammonia, are used as precipitants of the different metals, the quantity of sulphur may be easily ascertained. I took a given weight of sulphur, and converted it into sulphuric acid, by means of nitric acid. I then neutralized and evaporated it. Nitrate of barytes, poured in, gave a precipitate which, in one experiment, indicated a proportion of sulphur equal to 14,4, and in another to 14,6, contained in one hundred of sulphate of barytes. A difference so trifling need not be regarded. According to M. LAVOISIER, sulphuric acid contains 71 of sulphur, and 29 of oxygen; and, according to the synoptic tables of M. FOURCROY, sulphate of barytes contains 33 per cent. of sulphuric acid; therefore, by this calculation, one hundred of sulphate of barytes contain 23,43 of sulphur, instead of 14,4, or 14,6. I do not pretend to account for so great a difference in these results;† but that very difference led me (by exciting me to doubt those which I had obtained, and inducing me to frequent repetition,) to a more positive conviction of the proportions

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* See note in page 197.

† I was particularly cautious in ascertaining that, during that experiment, no sulphureous acid had been produced, the formation of which would have easily accounted for any difference.

I have mentioned. M. Lavoisier obtained his proportions by combustion; and, admitting even that nothing was lost, it must have been rather difficult to obtain the sulphuric acid in a state proper to value the quantity. Indeed I do not know of any direct experiments which prove, in a satisfactory manner, that we have ever obtained that acid perfectly free from water; unless when combined with an earth, or an alkali, in some salt, and that salt calcined in a very strong red heat.

To ascertain the quantity of metallic arsenic in mispickel, arsenical pyrites, &c. the most advantageous method is, to acidify it by nitric acid, and then to combine it with oxide of lead. This arseniate of lead (containing, as was before said, 33,2 per cent. of acid,) may be estimated to contain 22 per cent. of metallic arsenic. If both sulphur and arsenic are present, lead may be equally serviceable, after both have been acidified; for sulphate of lead is not materially soluble in any acid; whereas, on the contrary, arseniate of lead is very much so.

When copper and iron are to be separated, one single affusion of ammonia will not always suffice. That two may be sometimes necessary, is an objection to the method I propose, for the subsequent ebullition with potash. But, when I use that of precipitating the copper by iron, it requires no previous precipitation by any alkali. It is sufficient to add muriatic acid to the original solution of the ore in nitric acid, and evaporate to dryness. The nitric acid is dislodged from the oxide of copper, and the muriatic takes its place. If a single evaporation is not sufficient, a second (for the operation is very short, and causes no loss upon filtres, &c.) may be attempted; and, when the iron, used for the purpose of revivifying the copper, is put in, the liquor may be made to boil; by which means, the process is rendered much more certain and expeditious. Some iron will necessarily be dissolved; and the quantity must be noted. The liquor, which contained muriate of copper and of iron, now contains only the latter. Boiled with a little nitric acid, it will become red; and then ammonia, or potash, will give a red precipitate, which, well washed and dried, will represent 61 per cent. of metallic iron. All these metals having thus been precipitated, no constituent part of the ore, except the sulphur, which, in the first treatment, had been converted into sulphuric acid, is contained in the liquor; and from it, when neutralized, this latter may be precipitated by nitrate of barytes, which will represent 14,6 per cent. of sulphur. The absolute necessity of constantly using pure alkalis, in this method of analysis, is too evident to be insisted upon.

GENERAL VIEW OF THE FOREGOING ANALYSES.

In taking a retrospective survey of the experiments above related, upon the various natural arseniates of copper which we have examined, we shall find,

First, that natural arseniate of copper exists in three different states of combination; the first containing 14 per cent. the second 21 per cent. and the third about 29 per cent. of acid.

Secondly, that each of these may contain different proportions of water, either as constituting a hydrate, or as water of crystallization.

Thirdly, that, upon losing its water, arseniate of copper will pass from blue to pale green, and finally to brown, as in No. I.

Fourthly, that No. I. is the only real arseniate of copper, all the others being arseniates of hydrate of copper.

Fifthly, That No. I. is not to be admitted as an arseniate of copper containing 39,7 per cent. of acid. For, if we put it on the same footing with the others, in admitting a due proportion of water into its composition, we shall, by calculation, reduce it to that class containing 29 per cent.

Sixthly, That, in beginning with that kind which contains the least quantity of acid, and rising progressively to that which contains the greatest, we shall find the order to be thus:

No. VI. contains - - - - 14 per cent.
No. V. - - - - - - - 21 per cent.
Nos. I. III. and IV. - - - 29 per cent.

No. II. seems to be a particular species. It consists of a much greater proportion of oxide, with a less quantity of water, (and this its external colour announces,) combined with nearly the same proportion of arsenic acid. Indeed, if certain characters did not speak so strongly in favour of this division, I should not have hesitated to class it with the last mentioned kinds. But it is found in many states, which seems to indicate, that the water is by no means in the same degree of intimate combination that it is in the others; and this alone may serve to distinguish it, to the eye of the mineralogist.

If, to the above natural arseniates, is added the second artificial arseniate, we shall have another proportion of acid, at the rate of 40 per cent. Here then we have two simple substances, combined in four different proportions, and producing seven distinct combinations.

But, what is not the least to be admired, is the wonderful accordance in the order which two sciences, operating with very different instruments, have allotted to the same substances. By that, not only the sagacity of Nature becomes very striking; but, from the acknowledged accuracy of one method of investigation, the reliance to be placed upon the other is rendered more conspicuous; and each receives additional strength and confirmation. Chymistry has long been in the habit of aiding the science of mineralogy, of which it laid the foundation; but it was not till lately, that crystallography could form a judgment of its own, much less confirm the truth of the source from which it sprung.

SECTION II.

ARSENIATES OF IRON.

The arseniates of iron remain now to be examined. Included, formerly, among arseniates of copper, they have been separated from them, upon the authority of chymical analysis. For, although to recognize, by external character and form in all their modifications, substances already known, is particularly the province of crystallography; yet he, who would expect that it should declare the nature of those substances which it beholds for the first time, would exact more than it ever has promised, or ever could perform. Among fossils, it may class, and find new species; but chymical analysis is the basis of all arrangement, among metallic ores. In them, to separate, is the task of the one; to assign a place, is the business of the other.

Cupreous Arseniate of Iron.[*]

One hundred parts of this arseniate, exposed to a low red

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[*] This species had been mentioned by Mr. PROUST; but in a manner which, as it was a new substance, and demanded particular attention, does not give all the

heat, lost 12, which were pure water. Nitric acid was poured upon the residuum; and, finding that it was dissolved with difficulty, the ebullition was continued during several hours. The liquor was then filtered. 60 parts, which shall presently be examined, remained undissolved. Into this filtered liquor, nitrate of lead was poured, which occasioned a precipitate as usual; but the operation was discontinued, until I should obtain all the arseniate of copper which I imagined to be contained in the ore. For this purpose, I had recourse to the 60 parts mentioned above. They were in the form of a greenish grey powder, very hard and gritty, which had every appearance of silica, contaminated by a small portion of copper interposed between the molecules of that earth. I resolved to treat it in the same manner as all siliceous stones, and proceeded to boil it with potash.

In less than three minutes, it became of a very red brown, from the greenish grey which it originally was; and seemed considerably attenuated in its particles. The liquor was decanted, and examined. It was found to contain arsenic acid; and the precipitate, which had resisted the action of the potash, was proved to be a mixture of iron and copper.

These preliminary experiments were sufficient to indicate a ready method of analysis. 100 parts, boiled with potash, immediately became of a deep reddish brown. The liquor was separated from the residuum by filtration; and, after the usual

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satisfaction which that chymist generally affords. No doubt, the scarcity of the ore prevented his making every necessary research; and I may deem myself fortunate in having been so near the spot in which it is found. My friend, Mr. HATCHETT, very obligingly gave me a specimen of this ore which he had received from Dr. PALLAS, who had brought it with him from Siberia, where it had been found.

neutralization, evaporation, and affusion of nitrate of lead, (all of which operations were detailed in the first part of this Paper,) gave a precipitate, corresponding to 35,5 of arsenic acid. The first residuum weighed 53. Dissolved, as far as they could be, in muriatic acid, there remained 3, which, upon examination, were found to be really silica. Ammonia, poured in excess into the muriatic solution, redissolved 22,5, which were copper; and 27,5 of iron remained behind. The proportions were,

Silica - - - -	3
Arsenic acid - - -	33,5
Oxide of iron - - -	27,5
Oxide of copper - -	22,5
Water - - - -	12
	98,5

None of these experiments were sufficient to determine, whether this ore is in the state of a triple salt, or merely a mixture of two arseniates. As, in a ternary combination, the proportion of acid might vary, it cannot be justly called in to aid us in our enquiry. The solubility of one part of the ore being much greater than that of the other, and in different quantities of each salt, incline more to the opinion, that it is but a mixture.

Simple Arseniate of Iron.

This arseniate, exposed to any degree of heat, gave but an unsatisfactory result, with regard to the quantity of water. The arsenic acid is volatilized from this ore, with peculiar facility, for which I shall attempt hereafter to account.

Some subsequent experiments, however, have induced me to fix the quantity of water at about 10,5.

One hundred parts, boiled with potash, left 58,5. The liquor, treated as usual, by nitrate of lead, gave 31 of arsenic acid. The 58,5 left four, which muriatic acid could not dissolve, and which were silica. Ammonia dissolved 9; and there remained 45,5 of iron. This analysis presents the following result:

Silica - - - -	4
Arsenic acid - - -	31
Oxide of iron - - -	45,5
Oxide of copper - - -	9
Which will leave for Water	10,5
	100,0

This ore appears to be a pure arseniate, mixed accidentally with a little copper; as some of the copper arseniates casually give traces of iron. This is the kind mentioned by Mr. KLAPROTH, as an arseniate of copper, and the first known under that denomination. Heating it on charcoal, before the blow-pipe, he perceived a smell of arsenic, and, at length, obtained a metallic button, which was found to be copper. That there is copper in this ore, is evident from analysis. But the mere arsenical smell, was not a sufficient ground to assert that it contained arsenic acid; for this metal might, with as much probability, have been in any other state. If indeed, that very accurate and able analyst had, upon trying the ore with the blow-pipe in a platina spoon, perceived no fumes, he might then have concluded, that the arsenic must be in the state of acid, and that charcoal was necessary to operate a partial reduction, to which the arsenic owed its volatility and its smell. But no such experiment is reported.

It is also rather extraordinary, that Mr. GMELIN should have taken this ore out of the class of arsenical ores, and left it as an unknown species of copper; when, in fact, it is an arsenical ore, but not an arsenical ore of copper.

I examined some crystals, which are commonly attached to the specimens of this ore. They were those which, according to M. DE BOURNON, are in a state of decomposition. By this spontaneous decay, they become of a deep brownish red, not unlike the substance called colcothar; but they still retain their cubic form. They contain a little acid and water, owing perhaps to their having escaped from total decomposition. The same theory that accounts for the difficulty of ascertaining the quantity of water, will account for the red colour they thus assume.

When green sulphate of iron is exposed in a crucible to a red heat, it is well known that sulphureous acid is disengaged in great quantities; and that, if the operation is continued long enough, there remains a red powder. In this case, the green oxide of iron has taken up oxygen, from the acid; and this latter has been partly decomposed, and almost totally volatilized. Now, in the species here spoken of, the iron, as in the green sulphate, is in the state of green oxide; therefore, capable of receiving an additional portion of oxygen. But arsenic acid will, at a high temperature, lose a part of its oxygen, and, retrograding to the state of white oxide, will be volatilized; and still more easily will those changes take place, when oxide of iron, ready to receive, and arsenic acid, ready to yield oxygen, are in contact. A less degree of heat, therefore, will suffice to drive off this acid, from green arseniate of iron, than from arseniate of copper. But we must not from this conclude, that the affinity of the latter metal for arsenic acid is superior to that of the former; for, the attraction of green oxide of iron for oxygen, and of caloric for white oxide of arsenic, determine a new order of divelling affinities.

But, most of the mineral acids that have been tried, have been found capable of uniting with iron in two states; in the state of green oxide, and in that of red oxide, the residuary powder above-mentioned. I was desirous to know whether I could, in any manner, imitate by art, the last natural products I have examined, as I had already imitated, in some degree, an arseniate of copper. For this purpose, I decomposed green sulphate and red sulphate of iron, by arseniate of ammonia; and, having well washed and dried the precipitates, proceeded to examine them.

The green arseniate was acted upon by heat, in the same manner as the natural one, and exhibited the same appearances. By the usual methods, I found its proportions to be,

Oxide of iron - - -	43
Arsenic acid - - -	38
Water - - - -	19
	100

This is not the same proportion of acid that is contained in the natural arseniate; however, I state them both as I found them. The other artificial arseniate, which is of a pale greenish red, afforded,

Red oxide of iron - - -	36,5
Arsenic acid - - - -	41,5
Water - - - - -	20,0
	98,0

These salts agree with the generality of the known salts of iron; all of which contain a greater quantity of oxide, as the oxide itself contains less oxygen.

By boiling with nitric acid, it was easy to convert the green arseniate of iron into the red; and such is the case with all the salts of green oxide of iron. As, during the course of these experiments, I had occasion to make some remarks upon the divers habitudes of this metal, which, as far as I know, have not all been observed, I shall terminate the whole of these analyses (as I have already done that part of them which treats of arseniate of copper in all its known varieties) by simply stating what has occurred to me.

I happened to boil some muriatic acid upon a greater quantity of iron than the acid could dissolve. I found a perfectly limpid and colourless liquor remain, which, nevertheless, was a solution of muriate of iron. This colourless liquor being decomposed by arseniate of ammonia, the precipitate was of a greenish white, and soluble in a great quantity of water; but, passing to a much deeper green, quickly fell to the bottom. A prussiate, or a gallate, poured into the said solution, occasioned no change, till it had stood a considerable time exposed to the contact of the air. By potash, and by soda, a white precipitate was thrown down, which quickly assumed a green tinge; and that tinge increased so much as to become a very deep grass green, in a few minutes. Ammonia occasioned a white precipitate, which was redissolved by an excess of the precipitant. The ammoniacal solution assumed the same greenish tinge, and speedily deposited an oxide of iron, which was first of a deep green, but instantaneously became black, with some yellowish ochrey particles on the surface. If, however, these precipitations were effected in a bottle well stopped, and defended from the contact of the atmosphere, no change of colour took place; and that portion which was dissolved by an excess of ammonia remained in the solution. In endeavouring to distil, or to evaporate, the water of this colourless solution, in order to obtain crystals, it became of a light green, the intensity of which augmented, as the distillation was continued. I could not, therefore, hope to procure this salt in a crystalline form. Hence, it is evident, that we have a white muriate of iron, which, as well as the oxide it contains, is very susceptible of assuming an addition of oxygen; for, to that alone I attribute the precipitation caused in a solution of that salt, into which the different reagents above-mentioned had been poured; a precipitation which did not take place, till after it had been exposed in a situation where it could absorb the quantity of oxygen necessary to produce a change in its principles.

This solution of white muriate of iron, when exposed to the air, becomes green, and is then in the state of green muriate, well known. At a certain degree of oxidation, I have observed the precipitate formed, to be soluble in the carbonates of potash and of soda, and still more so in that of ammonia; but, upon absorption of oxygen, to be quickly abandoned by them, and then to fall to the bottom, in a blackish powder mixed with yellow. If, into a solution of green muriate of iron, nitric acid is poured, both liquors being cool, and not too concentrate, the muriate will become of a blackish brown, not unlike malate of iron. Precipitated by the alkalis, it yields a black powder, no longer soluble in them; but which resembles, in every respect, common black oxide of iron.

If this green muriate of iron is further exposed to the air, the liquor becomes red, but still gives a blackish green precipitate; but, if it is boiled with nitric acid, it then is converted into a red liquor, which yields a red precipitate, by all the alkalis and earths capable of causing a precipitation. From these observations, upon the different combinations of iron with oxygen, and of oxide of iron with muriatic acid, some conclusions may be drawn, interesting to mineralogy as well as to chymistry. The variety of colour in many stones in which iron has been found, is a fact which, although we cannot deny our assent to direct experiments, has never been accounted for in a satisfactory manner. In white, green, yellow, black, red, in a word, in fossils of every colour, iron, with sometimes the help of manganese, and lately of chromium, has been regarded as the colouring matter of every shade; but it seems almost paradoxical, that the same substance should assume and communicate so many tints. In mica, kaolin, amianthus, asbestos, rock crystal, and all white stones, I believe it to exist as the white oxide; and that state is its first degree of combination with oxygen. In them, this metal is not very abundant; for, if it were, I have some reason (as shall be proved immediately) to think, that they would obey the loadstone strongly. In lapis ollaris, serpentines, and many green stones, we have the green oxide; and most of these are magnetic; nay, as Mr. HUMBOLDT has observed, serpentines enjoy the property of polarity. And thence I conclude, that the rarity of this metal, in the first class, prevents them from participating that quality. This, I believe, to be its second stage of combination with oxygen. In the state of black oxide, it is frequently found, and is too well known to need further comment. I believe this to be its third stage of oxidation. But there is a red liquid muriate, which gives a very dark greenish precipitate, approaching to dark brown. What the state of that precipitate is, I have not yet determined; but I imagine it to be a mixture of black and red. Brown and yellow oxides, I am confident, are mixtures of simple oxides, and neither of them is an oxide *sui generis.* The red oxide is the extreme of oxidation; and affords many beautiful colours in nature and in art.

It is much to be desired, for the advancement of analytic chymistry, that experiments upon the proportions of oxygen with which metals are capable of uniting, under different circumstances, and upon the combination of those oxides with all the known acids, together with many others of their properties, would attract the notice, and engage the labours, of accurate manipulators. Experiments of this kind have been despised, from an idea of their resembling a mere mechanical employment; but, so far is that from the truth, they may justly be considered among the most difficult problems of chymistry; and it is only from the rigid and constantly similar results of such experiments, that we can hope to attain an intimate knowledge of the principles with which nature has originally operated.

SECTION III.

ANALYSIS OF THE RED OCTAEDRAL COPPER ORE, IN WHICH THE METAL EXISTS IN A STATE HITHERTO UNKNOWN IN NATURE.

In the course of the experiments which have been stated in the preceding sections, I have had occasion to examine a great number of copper ores, and particularly of copper ores from Cornwall; but, the only one which has afforded any interesting results, is the well known species called red copper ore, crystallized in regular and brilliant octaedrons. It has been so long known, and so often mentioned by mineralogists, that it may excite our wonder when we reflect, that its chymical nature has never been ascertained. For it would be an injustice to that very accurate and scrupulous analyst, M. VAUQUELIN, to suppose, that he meant to pronounce decidedly upon that point, by the single experiment which he had made,* and which is mentioned by the Abbé HAUY, in a short extract of his crystallographical arrangement of mineral substances, published in the *Journal des Mines.*

ROME' DE LISLE, the Baron de BORN, LAMETHERIE, the Abbé HAUY, and indeed every other mineralogist, concur in calling this substance red calx of copper; but some of them assert, that it contains a portion of carbonic acid. Among the many analyses which have been made of this ore, by FONTANA, MONNET, DE BORN, RENOVANTZ, and others, I could not find one, that in the proportions, or even in the ingredients, resembled what I had found to be its contents. The highest amount of copper, (that given by FONTANA,) does not exceed 66 per cent. and is far short of the real quantity. The remainder, as he states, consists of water, and of pure and fixed airs. The difference in the results I had obtained, together with some new facts, which I had occasion to observe during my experiments, induces me to treat the subject at some length; referring for its external characters, to those mineralogists above mentioned, who have amply described the ore, and confining myself entirely to its chymical analysis, and some analogous experiments.

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* He merely poured muriatic acid upon the ore; and, as it was entirely dissolved, without effervescence, concluded it to be an oxide, and not a carbonate, of copper.

One hundred parts of very pure and regularly crystallized red copper ore were reduced to a fine powder, and dissolved, without the assistance of heat, in nitric acid.

During the operation, a very violent effervescence, accompanied by a disengagement of nitrous gas, unusually copious and rapid, took place. When these phenomena had subsided, the solution was blue, like every other nitrate of copper; and the ore had entirely disappeared. The liquor, perfectly limpid, was evaporated to dryness: muriatic acid was poured in; and the nitric acid was expelled, by a second evaporation. Into the muriate of copper, which remained behind, a plate of polished iron was immersed, which, after the usual phenomena, gave a precipitate, that was found, upon examination, to be copper, and amounted to 88,5. In order to complete the hundred parts, it would be necessary to add 11,5. But fire expelled from the ore neither water nor any other volatile substance; nor did the weight of a given quantity appear either to diminish or to increase, by long exposure to a moderately elevated temperature. The only oxide of copper with which I was acquainted, as existing in nature, contains 20 per cent. of oxygen. I had therefore, 8,5 of copper exceeding the quantity I should have obtained, had the ore been wholly composed of black oxide of copper. And, on the other hand, as I had convinced myself, that no loss of weight had been occasioned by any part of the metal remaining unprecipitated by the iron from its solution, I could not conclude the ore to be in the state of native copper. I was led, therefore, to imagine, that it might be a mixture of those two substances; and that muriatic acid, by dissolving the one, and leaving the other untouched, would be the most effectual means of producing the separation I desired, and of determining the proportion of each.

Upon 100 parts of the ore, a sufficient quantity of strong muriatic acid was poured. A total solution was effected, accompanied with disengagement of caloric. The liquor was, at first, of a very deep brown, approaching somewhat to the tinge which water will receive, when strongly impregnated with the colouring matter of dried vegetable substances; but, upon being exposed to the air, and boiled some time, it became like every other muriate of copper; and a plate of polished iron precipitated 88 of metallic copper. From this last experiment it was evident, that no metallic copper was contained in the ore. But still the deficit, to be supplied by oxygen, amounted to no more than 12; while the copious disengagement of nitrous gas, in the first experiment, indicated that the metal was not at its maximum of oxidation; and the rapidity with which it seized upon an addition of oxygen, sufficiently shewed, how strong was the affinity of that principle for copper, in that particular state in which it exists in the ore.

I imagined it would be expedient to attempt some precipitations by other reagents, and make some further experiments. For this purpose, I dissolved some more of the ore in strong muriatic acid; and, when I thought that the acid had taken up as much as it could contain, and that the colour had arrived at its deepest tinge, I gently drew off the clear liquor, using all the precaution which the nature of the experiment allowed, to preserve it from the contact of the atmosphere, and proceeded to examine it. Knowing this solution of muriate of copper to be very concentrate, I attempted to dilute it; but, what was my surprise, when, upon the first affusion of water, I saw the liquor become turbid and milky, and a very abundant heavy precipitate, of a white colour, fall to the bottom.

Struck with the novelty of this appearance, I proceeded to collect as much of the substance as I could, in order to give it a thorough examination. For this purpose, I decanted the supernatant liquor, and continued to wash the precipitate. Upon every subsequent addition of water, I perceived that the precipitate lost a little of its whiteness, and drew towards an orange colour, not unlike the precipitates of platina. I soon found, therefore, that by this method I had no chance of obtaining, in a permanent and constant state, this muriate of copper, fit to be subjected to experiments proper to determine its internal nature and proportions. I then attempted to make use of alcohol, as precipitant, instead of water; but I found the salt to be soluble in it, when the excess of acid necessary for its solution in water was present. Nor was I more successful, when, after having precipitated by water, I washed with alcohol; for the colour of the salt passed gradually from very white to a shade of orange; less rapidly, it is true, in this case, but still so as to convince me, that I could not even thus procure, in a state constantly similar, the salt I wished to examine. The only conclusion which all these experiments entitled me to draw, was that, in the first instance, water precipitated the muriate of this particular oxide of copper from its solution, but in a manner very different from that in which muriate of antimony, of bismuth, and some other metallic salts are acted upon. When into either of these muriates water is poured, a precipitate ensues, but it retains a very small portion of acid, if any; whereas, in the case before us, it is a salt, and not an oxide of copper, that is thrown down. In order to effect, in this salt, a decomposition similar to that which takes place in muriate of bismuth, or of antimony, it is necessary to draw off the first liquor, and then proceed to wash copiously. The precipitate will by degrees assume an orange colour, which, as we shall presently see, is the real appropriate colour of this oxide of copper, prepared in the humid way.

It is evident also, from this precipitation, that this oxide of copper combines with muriatic acid by a very slender affinity.

As it did not appear to me, that I should obtain any thing very satisfactory from this combination with muriatic acid, I resolved to try some other acids. Sulphuric, phosphoric, oxalic, citric, acetic, tartareous, and acetous acids, were each poured upon known quantities of the ore, and kept in bottles completely filled and well stopped, in order to prevent any absorption of atmospheric oxygen. The liquors generally became blue; and, upon trial, were found to contain the common and well known salts of copper, composed of the respective acid, and the oxide of copper containing 20 per cent. of oxygen; while a large portion of the ore appeared to remain in its original state. But, as I was certain, that there could be no decomposition in most of these acids, under the above circumstances, and moreover, that no oxygen could be taken in from the atmosphere, it became a matter of no smallinte rest, to examine from what source the metal dissolved had acquired the necessary quantity of oxygen to favour its solution, and afford the usual salt of copper, in which it is oxidated in the proportion of 20 per cent.

I repeated, with all the above acids, the experiments tending to satisfy that enquiry; but, as the results from all were nearly similar, I shall mention that only which proved to be the most ample, and the most conclusive.

One hundred parts of the pulverised ore were introduced into a small phial, and dilute phosphoric acid was poured in, so as to fill it. A ground stopper closed it completely; and, in that state it was suffered to remain three days, during which time the bottle was frequently shaken. The acid became at first of a light blue, and increased in colour by remaining upon the ore. At the expiration of the above term, the liquor was decanted; the residuum was well washed and dried, and weighed 42. The blue liquor contained merely common phosphate of copper, held in solution by an excess of acid. Upon the 42 parts of residuum, strong muriatic acid was poured, which did not appear to produce the smallest change or effect. It was evident, therefore, that some previous alteration had been produced; for, if it had remained in its original state, muriatic acid would have acted upon it, as in the case already mentioned. To operate more effectually, nitric acid was added, and the whole gently heated. A complete solution followed, during which, much nitrous gas was disengaged. The remainder of the nitric acid was expelled by evaporation; and a plate of polished iron, immersed in this muriate of copper, afforded a precipitate of metallic copper, weighing within one part as much as the weight of the first residuum. It was evident, therefore, that a partial reduction of the ore had taken place; and, what is still more strange, had taken place by means of the presence of an acid.

In many observations which have presented themselves, in the course of various analytic experiments, something similar had before occurred to me. I have known metallic oxides yield a part of their oxygen, one to the other, in favour of some particular solvent. When the metallic oxide *A*, for instance, containing 25 per cent. of oxygen, is in contact with the metallic oxide *B*, containing 10 per cent. they will each remain quiescent in their respective states. But, if the solvent *C* comes to be added, and if the substance *B*, at 10 per cent. of oxygen, has no affinity for *C*, but at 15 or 20 per cent. has a very powerful affinity for it, then may the oxide *A* lend a part of its oxygen, in order to favour the combination of *B*, at 15 or 20 per cent. with the solvent *C*. Indeed, as soon as I saw the phosphoric acid assume gradually a blue tinge, and the undissolved powder begin to wear a more brilliant appearance, I imagined I should not fail to recognize the same fact in this case. When phosphoric acid has remained long enough upon the pulverized ore to dissolve all it can, the oxygen is concentrated, as it were, to the amount of 20 per cent. in the part which is dissolved; and all that which could not be dissolved has (through the twofold affinity of copper for oxygen, to the amount of 20 per cent. and of phosphoric acid for that oxide of copper, at that degree of oxidation,) yielded up its entire share of oxygen, to favour the combinations which take place in a new order, the only one which can exist among the substances now present. It is, therefore, to the disposing affinity,* caused by the presence of the phosphoric acid, which seeks to combine with black oxide of copper, that the reduction of 42 per cent. of this ore is entirely

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* As the term *predisposing affinity* has been objected to, I have used the term *disposing*, which I trust will not be thought improper. When in two bodies which, while together, remain in their original state, the equilibrium of their principles comes to be broken by the presence of a third, we cannot but allow, that it is this third which has disposed them to the rupture of that equilibrium; and, most certainly, be the fact explained as it may, whatever disposes may be called disposing.

to be attributed. All the acids above mentioned are capable of producing the same change, but in a manner, perhaps, not quite so distinct or satisfactory.

From the foregoing experiments it appears, that copper exists in this ore in a state hitherto unknown in nature; and that it contains much less oxygen than has ever been suspected in any oxide of copper; for, from the quantity which was precipitated in the metallic state by iron, it appears to be combined in the proportion of about 11,5 per cent. To confirm this idea, and ascertain as nearly as I could the precise quantity, I dissolved 100 parts in nitric acid; then boiled with potash, and filtered. One hundred and eleven remained upon the filter, which, as they had combined with a new portion of oxygen from the nitric acid, were in the state of black oxide, and correspond exactly to 88,75; so that I believe I shall be within one per cent. of the truth, in asserting the proportions to be,

Copper - - -	88,5
Oxygen - - -	11,5
	100,0

When, into a solution of muriate of suboxide of copper, liquid potash or soda is poured, a bright yellow precipitate, not unlike the precipitate of platina, takes place. This precipitate differs only in colour from the original ore; for it is soluble in muriatic acid, and affords the same solution and precipitation by water, and the same appearance with alcohol. It is likewise soluble in nitric acid, but with disengagement of nitrous gas, and gives the same appearances with the other acids above enumerated. The difference of colour seems to arise merely from the tenuity of its molecules, compared to the mechanical pulverisation of the natural oxide. When alone and dry, it is much more permanent in its nature, than when combined with muriatic acid; but any part of it that happens to be in contact with a filter, becomes green, and then blackish, leaving a mark of the same shade upon the paper. Were it not for this property of changing, it might be of use in the art of painting; for the colour is extremely beautiful, and would be highly valuable, if durable.

The precipitate caused in the muriate of copper, by the carbonates of potash and soda, is of a brighter yellow, and is a real carbonate of suboxide of copper. But, if ammonia is poured, at first in a small quantity, into the above solution, the precipitate is blue; and, upon adding an excess of the precipitant, the whole is redissolved, and the liquor is like any other ammoniacal solution of copper.

In order, however, to determine in what state the copper was dissolved by that alkali, I poured some ammonia upon 100 parts of this suboxide, in a well-closed phial. The liquor became blue; and I expected to find that part of the ore had been reduced, as with phosphoric acid; but the residuum was entirely soluble in muriatic acid, with the usual phenomena.

A spirituous tincture of galls, poured into muriate of suboxide of copper, afforded no precipitate, owing, I suppose, to the excess of acid; but, sulphurated hydrogen gas threw down a black, and prussiate of ammonia a lightish brown, precipitate.

I endeavoured to obtain muriate of suboxide of copper, by evaporation, and by distillation in a retort; but, as I could perceive the liquor constantly assume a bluish tinge, I could not reckon upon the purity of the salt, sufficiently to submit it to analysis.

Such were the principal experiments, which the fleeting and precarious existence of the salt allowed me to make upon it. But, from some properties which I had remarked, I could perceive that this ore was a natural oxide of copper, nearly in the same state as that artificial oxide which M. PROUST had found in the white muriate of copper, obtained by pouring a recent solution of muriate of tin into a solution of muriate of copper.

If, however, by the very nature of the substance, (which, as I saw it ever changing, I thought it would be loss of time to examine farther,) I have been turned aside from more certain results, I have been more successful in imitating by art the state of this natural product.

By exposing oxide, hydrate, or carbonate of copper, without addition, to a violent heat, in an open crucible, I frequently obtained the suboxide, which then presented all the properties already recognized in the above species of copper ore. In one instance, I so far succeeded, that, upon the very first inspection, the well experienced eye of the Count de BOURNON, recognized a lump of it to be a mass of semi-fused, artificial, red copper ore.

But I have found a method of producing at pleasure, in the humid way, all the new salts, and the oxide above described. As I had found about 11,5 per cent. of oxygen to be the quantity contained in the ore, I took that quantity of black oxide of copper which corresponded to 11,5 of oxygen; (57,5 of black oxide was the proportion thus indicated;) on the other hand, I took 50 parts of metallic copper, which had been precipitated by iron from muriate of copper, and which was in a state of tenuity not inferior to the finest powder. These were well mixed, by trituration in a mortar, and put, with muriatic acid, into a well stopped phial. A violent disengagement of caloric took place; the liquor became of the same colour as with the ore, and contained a salt, in every respect similar to that afforded by the ore; while a portion of metallic copper remained, with all its lustre, at the bottom of the phial. The solution was decanted; and the residuum of metallic copper weighed 7,5. Consequently, 42,5 had been dissolved, which, with 57,5 of black oxide, complete the hundred parts.

No experiment could prove, in a manner more satisfactory, the quantity of oxygen contained in 100 parts of this suboxide; nor could any afford results more important, or more conclusive. The passage of a portion of oxygen from one part of the metal to another, to favour its solution, as already stated, is proved beyond the possibility of doubt; and is doubly interesting, as it is the inverse of what happens to the ore when treated by phosphoric acid.

In the experiments of M. PROUST, he has estimated the quantity of oxygen, contained in 100 parts of this oxide, to be 17. This proportion was calculated upon the deficit of a single analytic experiment, made upon the salt of muriate of suboxide of copper, after having determined the quantity of acid, of water, and of metallic copper. But, first, the salt cannot easily be obtained (as I have before observed) in a state sufficiently certain to be relied on, in an experiment of this nature; and, in the next place, it is probable, as happens in almost every analysis, that the deficit was greater than the real quantity of oxygen. For, the agreement between the analytic and synthetic experiments I have just stated, seems to confirm 11,5 to be more exactly the proportion.

When, in the dry way, the above proportions of metallic copper and of black oxide of copper, or, when metallic copper with a corresponding proportion of hydrate or of carbonate of copper, were intimately mixed, and heated at a low red heat, the oxygen seemed to be equally distributed through all the mass; and every particle seemed perfectly homogeneous.

In the ore here spoken of, it is by no means rare to find large pieces of real native copper; and, whether we consider it mineralogically or chymically, it certainly is an interesting substance. But, how much more will it be esteemed, if it is regarded with a view to public utility.

The Baron de BORN has mentioned a grey cupreous pyrites, which, he says, contains 90 per cent. of copper. I have analyzed a similar one from Cornwall, (grey vitreous copper ore, page 203.) which I found to contain 86 of the same metal. But, if we reflect, not so much on the quantity as upon the extreme purity of this copper, and the wonderful facility with which this useful metal may be extracted, it will be found much superior to every copper ore hitherto discovered. It would be well worth the attention of miners, to keep a constant look out for this substance, which, I am informed, is not rare in Cornwall. It contains no iron, and no sulphur; the absence of which latter is a peculiar advantage. It is a fact not generally known, I believe, that there is hardly such a thing in commerce, as copper which does not contain a little sulphur; at least I have rarely met with any such; and it requires but a very minute portion of sulphur, to increase the fusibility of copper. The advantage of obtaining copper free from sulphur, is too obvious to require to be pointed out; and that advantage does this ore possess.

To work it separately, if ever it should be found in sufficient quantity, would well repay the labour it would cost; and a very small mixture of any disoxidating substance would, in a short time, reduce immense quantities.

From the foregoing experiments we may perceive, into how many errors we may be drawn, if, in arguing from the results which we obtain, we pronounce too hastily upon the state in which a substance exists, in the subject of any analysis. After what has been shewn, with regard to the action of muriatic acid upon a mixture of metallic copper and black oxide of copper, both reduced to powder, and of the action of phosphoric acid upon the ore itself, it may be still a doubt, whether this ore is really a suboxide, or a mixture of metallic copper and oxide of copper, at 20 per cent. of oxygen. But, as similar proportions of both, after having been made red hot, presented all the properties and appearances of the ore, much more strongly than when simply mixed, it is fair to conclude, that it is a real suboxide. Had not muriatic acid been used, the natural conclusion would have been, that the ore was a mixture, or at most a combination, of these two substances; for, such did it appear to be, by the testimony of the other acids. The truth is, we are but little acquainted with the exact state in which substances exist, in many natural combinations. However, in the mineral kingdom, such fallacious conclusions are less frequently to be dreaded, than in the vegetable and animal kingdoms. But, in every research, it is important to leave as little room for them as possible; and he who would indicate a sure and constant method of ascertaining whether, in many cases, what we deem a component part is not in fact a product of the operation, would render to science a service, the real value of which is, perhaps, not now entirely foreseen.