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Jacob Berzelius M.R.A.

To cite this article: Jacob Berzelius M.R.A. (1814) XXXII. An attempt to determine the definite and simple proportions, in which the constituent parts of unorganic substances are united with each other , Philosophical Magazine Series 1, 43:191, 161-175, DOI: [10.1080/14786441408637995](https://doi.org/10.1080/14786441408637995)

To link to this article: <http://dx.doi.org/10.1080/14786441408637995>



Published online: 27 Jul 2009.



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XXXII. *An Attempt to determine the definite and simple Proportions, in which the constituent Parts of unorganic Substances are united with each other.* By JACOB BERZELIUS, Professor of Medicine and Pharmacy, and M.R.A. Stockholm.

[Continued from p. 101.]

II. LAWS FOR THE FORMATION OF SUBSALTS.

EVERY chemist knows what is understood by neutral salts; but it is by no means easy to give a good definition of what is properly *neutral*. If we take that condition of alkaline salts, in which both the acid and the base are perfectly indifferent, so as to produce no reaction on vegetable colours, as an example of neutrality, it seems that we ought to consider those salts only as neutral, in which the same quantity of oxygen in the base combines with the acid, as in these alkaline salts, and which in double decompositions would set neither acid nor base at liberty. Davy, in his Essay on Electricity as a chemical agent, calls every combination *neutral*, in which the original electric reactions have ceased. This is in fact the only correct and scientific conception of a neutral combination; but it is only relative. For, according to this determination, the oxygen in the protoxide of lead, for example, must be neutralised; it no longer acts on the greater number of bodies as a [negatively] electrical substance, yet still retains the same relation to more combustible bodies, for instance, to potassium. Exactly the same is true of neutral salts. While potass and soda saturate a quantity of sulphuric acid, which contains three times as much oxygen as themselves, so completely, that the acid loses its powers, this is by no means the case with the protoxide of zinc, the oxide of iron, alumina, or zirconia. The attractions of these bases being extremely weak, every substance, which comes into contact with the salts, makes an effort to deprive them of a part of the acid: hence the action of the acid is still perceptible, and the salts appear not to be neutral, although they are the most neutral combinations of which the bases are susceptible. We are accustomed to call them *super-salts*, because the acid possesses the strongest powers, and consequently exhibits its effects most distinctly on the taste, and on vegetable colours. But when we consider the combinations of the weaker acids with the stronger bases, we find, that the base always exhibits its powers the most obviously. Thus, for example, the common deliquescent carbonated potass is sometimes called a subsalt; although the carbonic acid is united in it with the same quantity of oxygen, as in the carbonate of baryta or of lime, and these three salts are consequently in the same com-

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parative

parative state of saturation. And that both these earthy salts are neutral, appears 'from the sufficiency of the force of cohesion in both to prevent the predominant actions of their very powerful bases.

We may therefore, I believe, consider all those earthy and metallic salts as *neutral*, in which the acid is united with as much of oxygen in the base, as is found in another decidedly neutral combination of the same acid with an alkali or an alkaline earth. Thus, I consider as neutral all those sulphates, in which the base contains one-third as much oxygen as the acid; and all arseniates, carbonates, muriates, and phosphates, in which the base contains half as much oxygen as the acid. Salts in which there is more oxygen than this in the acid, I call *supersalts*; and *subsals*, those in which there is less.

In the first series of my experiments on definite proportions, I have adduced two examples of subsulphates. I thought that I had found that in the *subsulphate of the oxide of iron* the acid was combined with four times as much of the base as in the neutral salt, an opinion which appeared to be confirmed by a superficial examination of the *subsulphate of the oxide of copper*. But as I obtained more correct ideas on this subject, it appeared that the rule for the relation of the oxygen of the acid to that of the base by no means agreed with this determination: for, if the result of the analysis had been correct, the oxygen of the acid would have been $\frac{1}{4}$ of that of the base, and neither an integral multiple nor a submultiple. I therefore repeated the analyses with greater accuracy.

1. *Subsulphate of the Oxide of Iron.*

I dissolved some red oxide of iron in concentrated sulphuric acid; I heated the mixture until the acid was completely saturated, then dissolved the salt in water, filtered the solution, decomposed it with caustic ammonia, but so as not to precipitate the whole of the oxide, and digested the fluid for 24 hours upon the precipitate; which was then washed on a filter, as long as the presence of any sulphuric acid was indicated by the test of a salt of baryta. The salt, when well dried, had completely the appearance of the common precipitated oxide. When deprived of its water over a spirit lamp, which expelled from it nothing but pure water, it left a red powder, exactly like the colcothar of vitriol. Ten grammes of this powder, strongly ignited, left behind 7.98 of oxide of iron, and disengaged sulphurous acid during the operation: the remaining oxide, dissolved in muriatic acid, and tested with a salt of baryta, afforded no perceptible trace of sulphuric acid.

In this subsalt, therefore, 20.2 parts of sulphuric acid were united

united with 79·8 of oxide of iron, containing 24·47 of oxygen, while the acid contained 12·12; or, without any material error, half as much as the oxide. We see therefore that in the subsulphate of the oxide of iron the acid saturates six times as much of the base as in the neutral sulphate; for, according to the analysis of the neutral sulphate, which I have already described, 100 parts of sulphuric acid saturate 65·5 of the oxide of iron, and $65·5 \times 6 = 393$. But, according to the present analysis of the subsulphate, 100 parts of the acid are combined in it with 395 of the oxide; and the difference is so small that it can only be attributed to an error of observation.

I then collected a quantity of orange-yellow ochre, which had formed itself from a vitriolic solution in a vitriol work; I washed it carefully, and dried it in the sun. When the water was expelled over a spirit lamp, it had lost 21·7 per cent. By ignition it lost 15·9 per cent. more of sulphuric acid, and the remaining red unmagnetical oxide amounted to 62·4 per cent. According to this experiment, 100 parts of sulphuric acid combine, in the subsalt, with 392·52 of the oxide, and the yellow ochre is thus constituted:

Sulphuric acid.....	15·9	100
Oxide of iron.....	62·4	392·52
Water	21·7	

The quantity of water contains 19·15, the oxide of iron 19·13, and the sulphuric acid 9·54 parts of oxygen. Consequently the base and the water contain equal quantities of oxygen, and the acid exactly *half* as much oxygen: so that, notwithstanding the great difference in their appearance, the *yellow ochre* and the *brown red precipitate* are exactly the same combination. I am sorry that the former analysis was made at a time when I had not begun to collect any observations respecting the water of crystallization.

I was not a little anxious to know why this result differed so much from my former analysis of the same salt, and therefore prepared some more of the compound in the manner which I had then employed; dissolving some iron in diluted sulphuric acid, to which, for the sake of increasing the quantity of the oxide, I had added a little nitric acid. When nothing more was dissolved, I put, in order to expedite the separation of the subsalt, a piece of polished iron into the filtered solution, and exposed it, in an open vessel, to a temperature of 25° or 30° [77° to 86°] for several days. I thus obtained a considerable quantity of an ochre-coloured powder, possessing the characteristic property of the subsulphate of iron which I first analysed; it was very little soluble in muriatic acid, and when dried scarcely at all so, and was not altered by caustic potass. When I first dried this powder,

der, after washing it well, in the sunshine, and then heated it in a small glass retort, I obtained in the receiver some water strongly impregnated with ammonia, amounting to 18.5 per cent. By ignition 32 per cent. of sulphuric acid was expelled, and 49.5 per cent. of red unmagnetic oxide was left behind. It appears therefore that, in my earlier experiments, the nitric acid, which I had employed for oxidating the iron, and which I then thought it unnecessary to mention particularly, had produced a combination of a totally different nature from the pure subsalt; and I had, in all probability, examined a mixture of these substances. This *ammoniacal combination* is very remarkable; it appears to be a *triple subsalt*, analogous to the ammoniacal copper. When heat is applied, the sulphuric acid, which had been in combination with the ammonia, unites with the oxide of iron, and the ammonia is set at liberty. This substance, in its difficult solubility in acids, and in its incapability of being altered by caustic alkalis, seems to approach in some degree to the triple combinations of ammonia with muriatic acid and tin, described by Davy, and to the combination with muriatic acid and phosphoric oxide. As I had probably obtained only a mixture of this substance with the subsalt of the oxide, I thought it useless to attempt a more correct determination of its component parts. But I shall endeavour on a future occasion to obtain the combination in a state of purity, and to examine the proportions of its constitution.

It is demonstrated by the analysis of the pure subsalt of the oxide of iron, that the relation between the iron and the sulphur, which I had inferred from my first analysis, is incorrect. We shall see in the following analyses, that in the subsulphates, the oxygen of the acid is either *equal* to that of the base, or an integral *submultiple* of it. And hence it will follow, that, in all the subsulphates, the sulphur is in such a proportion to the metal, that its quantity is an integral-submultiple of the quantity in the sulphuret at a minimum, or of the quantity in the neutral sulphate of the protoxide of iron. In the salt of the oxide of iron here described, the proportion of the sulphur to the iron is exactly *one-fourth* of the quantity in the sulphuret at a minimum, and in the sulphate of the protoxide.

I must here call the attention of the reader to a circumstance, which is of the highest importance for the completion of the doctrine of definite proportions in mixtures, and without attending to which, we can scarcely hope ever to see the doctrine of the combination of organic bodies sufficiently illustrated: that is, to the existence of the *absolute minimum* of the combination of one substance with another, of which all other combinations must be multiples. Since only very few degrees of combination can exist between two bodies separately, that is, without the inter-
vention

vention of one or more other bodies; and since these perhaps never, or at least very rarely, exhibit combinations at a minimum, we are obliged to seek for these minima in more complicated modes of combination. It will be difficult to discover the true minimum; but every good experiment, made with this view, will be productive of interesting consequences. The subsalt of iron, just analysed, may serve as an example in illustration of this remark. If we should hereafter discover no combination of the sulphuric acid with a greater quantity of iron in the salts of the protoxide or oxide, and should the proportion of the sulphur to the iron, found in this experiment, be the greatest common divisor of all the numbers expressing the proportions which are found in the mixtures of sulphur with iron, we might be allowed to hope that we had found the minimum of sulphur with which iron could combine; 100 parts of iron here being united with 14.66 of sulphur. In the magnetical pyrites, called the sulphuret at a minimum, because it is the lowest stage of combination which can be separately exhibited, or in the neutral sulphate of the protoxide of iron, 100 parts of iron are combined with $14.66 \times 4 = 58.64$, in the sulphate of the oxide with $14.66 \times 6 = 87.96$, and in the common pyrites with $14.66 \times 8 = 117.28$ parts of sulphur. Consequently these are multiples of the lowest proportion by 4, 6, and 8, and we find that these multiples agree with the results of the experiments as far as the thousandths of the whole. It may be supposed that the multiple by 2, which is here wanting, still exists, although perhaps in a combination which is yet unknown; for instance, in a subsalt of an oxide, in which the sulphuric acid and the oxide contain equal portions of oxygen. If now 14.66 parts of sulphur were the smallest quantity with which 100 parts of iron could combine, it would follow, that no subsalt of the protoxide of iron could exist. But if, on the contrary, such a subsalt should be discovered, 14.66 of sulphur for 100 of iron would not be the minimum, and it could not be greater than 4.9, which would be the greatest common divisor of all the combinations of sulphur with 100 of iron. Nearly in the same manner I have attempted to find the minimum of oxygen in the combinations of carbon; but in order to discover which of the various numbers that might represent the quantity of oxygen, is the true minimum, a great number of experiments would be necessary, which would require the labour of several years before they could afford a tolerably certain result.

2. *Subsulphate of the Oxide of Copper.*

I precipitated some sulphate of the oxide of copper with caustic ammonia, taking care not to throw down the whole of the oxide, and heated 10 grammes of the precipitate, well washed and

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dried,

dried, in a glass retort, over a spirit lamp, as long as any aqueous vapours were expelled. The salt, thus dried, had lost 14·5 per cent. of its weight. When I dissolved it in nitric acid, and added a salt of baryta to the solution, I obtained 8·55 gr. of ignited sulphate of baryta, corresponding to 21·28 per cent. of sulphuric acid. Consequently this salt consists of

Sulphuric acid	21·28	100
Oxide of copper	64·22	301·8
Water	14·50	

The sulphuric acid contains 12·74, the oxide of copper 12·66, and the water 12·87 of oxygen; so that each component part contains an *equal* quantity. Consequently in this salt 100 parts of sulphuric acid saturate *three* times as much oxide of copper as in the neutral sulphate.

3. *Subsulphate of the Oxide of Bismuth.*

Mr. Lagerhjelm found, in his experiments on bismuth, that, in the sulphate of the protoxide, the acid contains three times as much oxygen as the base. I therefore decomposed a quantity of the neutral salt by adding water to it, and washed the subsalt, which remained undissolved, by the addition of fresh portions of water. The salt, being long and thoroughly dried on a sand-bath, was then ignited in a crucible of platina, as long as a trace of sulphurous acid was disengaged. It had lost 14·5 per cent. of its weight, and consequently consists of

Sulphuric acid . . .	14·5	100
Oxide of bismuth	85·5	590

But this quantity of sulphuric acid contains 8·685, and the oxide of bismuth 8·66 of oxygen: consequently the acid saturates *three* times as much of the base, as in the neutral salt.

4. *Subnitrates and Subnitrites.*

I have already treated, in the Second Continuation of my Essay, of the subnitrate, subnitrite, subsubnitrate, and subsubnitrite of the protoxide of lead, and of the subnitrate of the oxide of copper; and I have shown how far they serve to confirm my opinion of the composition of nitrogen, as well as the laws which I have here laid down for the formation of the subsalts.

5. *Carbonate of the Oxide of Copper.*

Ten grammes of carbonate of the oxide of copper, precipitated at the boiling temperature, and dried in the sunshine, being ignited in a small glass retort, afforded in the first experiment 7·16, and in the second 7·17 gr. of black oxide of copper. A considerable quantity of water was collected in the receiver. Consequently this salt cannot contain so much carbonic acid, as
to

to constitute with it a neutral compound ; and the acid and the oxide must therefore contain *equal* quantities of oxygen ; and 71.7 parts of the oxide must take up 19.73 of carbonic acid : the remaining 8.67 must be water, containing 7.5 of oxygen. This quantity of the oxide contains 14.34 of oxygen ; so that the oxygen of the water is half as much as that of the base. The slight difference in the results must depend on a little accidental moisture left in the oxide, from the imperfection of the process of drying.

Carbonate of copper, precipitated from a cold solution, affords a very bulky powder, of a blueish-green colour : but when a boiling heat is employed, we obtain a heavy, fine-grained, yellowish-green precipitate. I at first considered these two precipitates as different carbonates, and attempted to collect the former, and to wash it with cold water ; but it was converted by this process, in great measure, into the heavier yellow-green substance, and I could not obtain it in a pure state. I had accidentally placed on the sand-bath some carbonate of the oxide of copper, precipitated the day before, and still remaining in the fluid : when the carbonic acid had been expelled from the fluid, I observed that the carbonate of the oxide of copper, next to the bottom, collected into masses, and became of a yellow-green, without the least appearance of effervescence ; and this effect extended by degrees upwards as the fluid became warm. The alteration in the form appears therefore to depend not on any alteration in the quantity of carbonic acid, but merely in that of water ; exactly as the carbonate of the protoxide of zinc, in a temperature below the boiling point of water, sets at liberty the water combined with it, and unites into heavier grains, and as the blue hydrate of copper, when the fluid is heated, separates from the water, and is deposited in the form of a black oxide. Other subsalts of copper also, which, when they are precipitated cold, are light and bulky, become heavier by the effect of heat, and assume a yellower colour.

6. *Submuriates.*

We have found by some of the former analyses, that the muriatic acid, in the submuriates of the oxide of copper and of the protoxide of lead, is combined with four times as much of the base as in the neutral salt. Since the muriatic acid must contain twice as much oxygen as the base by which it is neutralised, the oxygen of the acid in these subsalts amounts only to one *half* of that of the basis.

7. *Conclusions.*

From these experiments I think myself authorised in drawing the following inferences respecting subsalts.

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a.) The

a.) The oxygen of the acid in a subsalt may be either a sub-multiple, or a multiple, by a whole number, of that of the base.

b.) The quantity of a base, which is combined with a given quantity of an acid in a subsalt, can be a multiple of the quantity in the neutral salt by such a number only, as is capable of expressing the proportion of the quantity of the oxygen of the acid to that of the base. For instance, in the subsulphates, the base can only be a multiple by 3, 6, 9, of the quantity in the neutral salt, and not by 2, 4, 5, 7, 8. On the other hand, acids which contain, in their neutral salts, 2, 4, 6, or 8 times as much oxygen as the bases, may take up in their subsalts 2, 4, 6, or 8 times as much of the base as in the neutral salts; but not 3, 5, 7, or 9 times.

It still remains to be inquired, whether there exists a subsalt, in which the base is less than double that of the neutral salt; for instance, whether any subsulphate exists, in which the acid contains twice as much oxygen as the base, or a subnitrate, in which the acid contains exactly four times as much oxygen as the base.

III. LAWS FOR THE FORMATION OF DOUBLE SALTS.

The combinations which, in the first Antiphlogistic Nomenclature, were called *triple salts*, have been latterly more properly denominated *double salts*; being always composed of two neutral combinations; and they may commonly be obtained by mixing the solutions, and crystallizing them together.

These double salts may be of different kinds: containing either one acid and two bases; or two acids, or substances representing acids, and a single base. Of the former kind we are acquainted with several salts, of the latter with only a few, and with none very accurately.

1. *Double Salts of a single Acid.*

The principle of the formation of these double salts is not difficult to be found, since we know that most of the supersalts, if they are saturated with a second base, afford such salts, and it has been shown that the supersalts contain twice as much of the acid as the neutral salts. Consequently the new base must contain exactly the same quantity of oxygen as the base of the supersalt. For example, the soda, the protoxide of iron, or the protoxide of antimony, with which the supertartrate of potass is neutralised in pharmaceutical preparations, must contain as much oxygen as the potass, because it neutralises an equal quantity of the acid. We shall find from the analysis of alum, that the existence of the double salt, in these cases, depends not so much on the acid, as on the affinity of the bases; for alum cannot be obtained by saturating

turating the superfluous acid of the supersulphate of potass with alumina, unless the supersulphate be in great excess. Besides, certain bases afford double salts with almost all acids, although most of the acids are incapable of forming a supersalt with either of these bases. Thus ammonia, for example, affords double salts with magnesia, with the protoxide of manganese, with the oxide of copper, and with the protoxide of zinc; and we have great reason to think that these bases always observe the same relation to each other, containing *equal* quantities of oxygen. I shall adduce some few examples of double salts of the *first* kind, which may be sufficient to illustrate the law of their formation.

Sulphate of Ammonia and Magnesia.

Ten grammes of this salt, finely powdered, and dried in the sun, were heated in a platina crucible, and then ignited. They afforded exactly one-third of their weight of sulphate of magnesia, whence the magnesia is found to amount to 11.11 per cent. and its oxygen to 4.43 per cent. of the whole weight. I now mixed, with these 3.334 gr. of sulphate of magnesia, a quantity of sulphate of ammonia, in which the oxygen of the ammonia amounted to .443 gr. that is, 4.181 gr.: the two salts were dissolved in boiling water, and dried on a glass dish in the sunshine: their joint weight was found to be 10.006 gr. Consequently the sulphate of magnesia had taken up 2.49 gr. of water, containing 2.2 gr. of oxygen, that is, five times as much as either of the bases contained. But since the sulphate of ammonia contains water of crystallization of which the oxygen is equal to twice that of the base, the whole water of the salt contains seven times as much oxygen as that of each of the bases: and the respective portions of oxygen in the different substances entering into the combination are as 1, 1, 6, and 7.

Sulphate of Ammonia and the Oxide of Copper.

Ten grammes of this salt, finely powdered, and dried in the sun, were mixed with lime in a small retort, and the ammonia was expelled in the same manner as in the analysis of the sulphate of ammonia. The apparatus had lost .827 of its weight. Ten more grammes, dissolved in water, were mixed with about as much of the carbonate of potass, as was required for the saturation of the sulphuric acid, and then evaporated to dryness. When again dissolved in water, they left behind carbonate of the oxide of copper. The fluid, which had a slight excess of alkali, exhibited, by the test of sulphuretted hydrogen, a slight trace of copper. The oxide of copper obtained, weighed, after ignition, two grammes. These contain .3932 gr. of oxygen; and the .827 gr. of caustic ammonia .3897 gr.; so that the two bases contain
equal

equal quantities of oxygen. If now we compute the quantity of sulphuric acid necessary for their neutralisation, there will remain a quantity of water of crystallization containing seven times as much oxygen as either base. Consequently in this double salt, each of the two simple salts retains its appropriate water of crystallization, as appears from the respective analyses. The quantities of oxygen of the several component parts are here related, as in the former case, in the proportions of 1, 1, 6, and 7.

Alum.

Alum is generally considered as a double supersalt; but my analysis appears to show that it is in fact a neutral double salt.

Twenty grammes of pure alum were heated in a platina crucible, over a spirit lamp, till they lost no more of their weight. The swollen mass was compressed into the crucible, and at last covered, in order that the heat might pervade every part of it equally. It had now lost 9 gr. and I could find no trace of the escape of an acid, which must have been discoverable by the smell. Consequently alum contains 45 per cent. of water of crystallization. The dry salt was again dissolved in water, the assistance of heat being required for the solution; muriate of baryta was added, and the precipitate, when ignited, amounted to 19.973 gr. or very nearly to the original weight of the alum: so that, in a crystallized state, this substance contains 34.255 per cent. of sulphuric acid [; or, according to the corrected analysis of the sulphate of baryta, which appears to contain from 34.314 to 34.48 per cent. of sulphuric acid, at least 34.27 per cent. *Gilbert.*].

Ten grammes of alum were dissolved in water, and digested with an excess of ammonia: they afforded alumina, which, when well washed and burnt, amounted to 10.67 per cent. As this did not agree with Mr. Thenard's result, I repeated the experiment with 50 gr. of alum. After filtration, the fluid mixed with the excess of ammonia, and the water, with which the earth was washed, were evaporated to dryness, and redissolved in water, when they afforded a small quantity more of alumina: the whole, being collected and ignited, weighed 5.43 gr. and lost nothing more of its weight by repeated ignition. Consequently alum contains only from 10.67 to 10.86 per cent. of alumina.

Ten grammes of alum, dissolved in water, and digested in a small glass flask with carbonate of strontia, as long as any effervescence existed, and then with new portions of the same carbonate added in excess, were deprived in this manner of the whole of the sulphate of alumina. The precipitate was not swollen, as might have been expected from the alumina, but heavy and easily washed. The fluid, when filtered, was not alkaline,

nor

nor did it become turbid upon the addition of ammonia. When evaporated, together with the water used for washing the powder, in a platina crucible, and ignited, it afforded 1·815 gr. of sulphate of potass, answering to ·981 gr. of potass.

Since we have seen that alumina contains about 46·7 per cent. of oxygen, it is impossible that the bases can here contain *equal* parts of oxygen. Alum, according to these experiments, is thus constituted:

Sulphuric acid ..	34·23	Or,	
Alumina	10·86	Sulphate of alumina	36·85
Potass	9·81	Sulphate of potass ..	18·15
Water	45·00	Water	45·00

Now, 9·81 parts of potass neutralise 8·37 of sulphuric acid, and 25·86 parts of sulphuric acid remain for the alumina: consequently the alumina saturates in the alum three times as much acid as the potass, for $8·37 \times 3 = 25·11$; so that the alumina must contain three times as much oxygen as the potass. But 9·81 parts of potass contain 1·674 of oxygen, and 10·86 of alumina 5·077; and $1·674 \times 3 = 5·022$. The 45 parts of water contain 39·71 of oxygen, and $5·022 \times 8 = 40·17$. It is true that this analysis is not correct to the last places of decimals: but it is at least sufficient to prove, that in alum the alumina contains three times as much oxygen as the potass; and in this instance we have a double salt, in which the oxygen of one of the bases is an integral multiple of that of the other.

Since the proportion of the alumina to the sulphuric acid, in this analysis, agrees as nearly as possible with that which was found in the neutral sulphate, it is impossible that alum should be a supersalt; but it is indebted for its acid properties to the weak attraction of the alumina to the sulphuric acid which belongs to it; the sulphate of alumina preponderating so much above that of potass, that it communicates to the compound almost all its outward characters.

Alum and the other double salts afford us interesting examples of the combinations of more than two oxygenized bodies. The potass here contains the smallest quantity of oxygen, which must therefore be the common divisor for the quantities contained in the other component parts. If we call this quantity 1, the alumina will contain 8, the sulphuric acid 12, and the water 24.

Finally, I must observe, that my analysis of alum differs in some measure from that of Thenard and Roard. These chemists found in alum $12\frac{1}{2}$ per cent. of alumina, and only 16 per cent. of sulphate of potass. [Vauquelin found the component parts always 10·5 of alumina, 10·4 of potass, 30·52 of sulphuric acid, and 48·58 of water: the acid and the water taken together agree nearly with Berzelius's result: the alumina is a little less, perhaps

haps from the same causes of error which affected Berzelius's first experiment. *Gilbert.*] MM. Thenard and Roard employed 489 grammes of alum, from which they obtained 61 or 62 of alumina, a quantity which, when moist, would occupy the bulk of ten pounds of water, and which must have been received either on a very large filter or on several small ones: in both cases, the washing it, and its separation from the paper, must have been subjected to great difficulties. It is also probable, that the separation of the sulphate of potass from the fluid obtained, by the addition of lime, could give no very correct result. Probably therefore the difference of our determinations is rather to be attributed to the more or less appropriate methods employed than to the experimenters. Besides, it is certain that an analysis on too large a scale can never afford a very correct result; nor do these gentlemen appear to have been in pursuit of very minute accuracy in their experiments.

A double Subsalt.

There exist also some double subsalts; but I have hitherto examined only one, that is, the combination known in pharmacy under the name of *cuprum ammoniatum*. In order to prepare this salt, I dissolved some sulphate of the oxide of copper in caustic ammonia, precipitated the double salt with alcohol, washed it again with alcohol, and dried it in the air. It is very difficult to observe with accuracy the moment of the attainment of perfect dryness; for the salt is decomposed on the surface, before the alcohol has been expelled from its internal parts; it then becomes by degrees of a sky-blue colour, and at the edge green. Hence it is impossible to obtain a very correct analysis of this salt; but it will not be difficult, with the assistance of the laws of combination which have been here developed, to discover its true composition, since the result of the analysis cannot deviate far from the truth.

I drove off the superfluous ammonia from a part of this salt, on a sand-bath, until it became quite gray; it had lost 20.33 per cent. in weight. When I repeated the experiment in a small retort, I found that a little water escaped at the same time. The gray powder, when water was poured on it, became first of a light blue, and then, as I gently heated it, of a dark-brown colour. This unquestionably depended on the decomposition of the salt, and the formation of a portion of neutral sulphate of ammonia and copper, while some hydrate of copper was first produced, and then decomposed by the application of heat. The solution had a faint blue colour, and left 40 per cent. of sulphate of ammonia, mixed with a small quantity of the double salt. The part undissolved, being a mixture of black and green oxide,
amounted

amounted to 48·7 per cent.: so that the products obtained weighed 9 per cent. more than the salt employed. This partly depends on the quantity of water of crystallization in the sulphate of ammonia, and partly on that of the new double salt.

In order to determine more correctly the composition of this subsalt, I dissolved 5 grammes of it in water, saturated the solution with muriatic acid, and precipitated the sulphuric acid with muriate of baryta. The precipitate, when washed and ignited, weighed in one experiment 4·685, and in another 4·7 gr., answering to 32·25 per cent. of sulphuric acid.

The superfluous baryta was thrown down with sulphate of soda, and then the filtered solution mixed with carbonate of potass, and evaporated to dryness. The mass, when redissolved, had an excess of potass, and afforded a greenish solution; the potass was nearly saturated with muriatic acid, and the carbonate of copper, received on a filter, washed, dried, and ignited. The liquid, still a little alkaline, exhibited by means of sulphuretted hydrogen a small residuum of copper, which being separately ignited, and weighed with the rest, made together 1·7 gr., or 34 per cent. of oxide of copper. We therefore find in this salt the same proportion between the acid and the oxide of copper, as in the neutral sulphate, and its properties as a subsalt are wholly dependent on the ammonia. But does the salt contain a quantity of ammonia capable alone of forming a neutral salt with the same quantity of sulphuric acid? I was at first persuaded that it did.

I mixed, in order to examine this, 5 grammes of the same salt in a small glass retort, with finely levigated lime, and decomposed it exactly in the same manner as I have related respecting the sulphate of ammonia. The little apparatus had lost 1·32 grammes, consequently the salt must have afforded 26·4 per cent. of ammonia. The 7·35 per cent. wanting must have been water, so that the *cuprum ammoniatum* is thus constituted:

Sulphuric acid	32·25
Oxide of copper . .	34·00
Ammonia	26·40
Water	7·35

This quantity of the oxide of copper contains 6·68, and the water 6·5 parts of oxygen, so that the oxide and the water are in the same proportion in this salt as in the subsulphate of the oxide of copper. The ammonia contains 12·424 parts of oxygen, or about twice as much as the other component parts; for we have seen that it is impossible to exhibit this salt in a state of dryness, without depriving it of a little of its alkali; so that the quantity must appear too small in this analysis.

It is evident that the two bases taken together here contain
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an equal quantity of oxygen with the sulphuric acid, that is, the oxide of copper one-third and the ammonia two-thirds as much. Consequently this salt is so constituted, considering both its bases, as to agree with the rule for a simple subsulphate. The quantities of oxygen are expressed by 1 for the oxide, 1 for the water, 2 for the ammonia, and 3 for the sulphuric acid.

It is not so easy to determine the nature of the alteration which the *cuprum ammoniatum* undergoes by exposure to the air. But it appears, when long kept in vessels imperfectly closed, so as to fall into a sky-blue powder, to lose half of its ammonia, so that the sulphuric acid then stands to each base in the same relation as in the neutral salts. When it is changed to a green powder, a still greater quantity of ammonia is lost, and the residue is a mixture of more or less dry neutral sulphate of ammonia with subsulphate of oxide of copper, accordingly as the alteration has been made by the effect of heat, or by exposure to the air. The green powder formed by heat is capable of supporting a temperature somewhat higher, without being decomposed, but afterwards emits sulphurous acid, sulphite of ammonia, water, and nitrogen, and leaves in the retort a fused dark-brown mass, which, when water is poured on it, affords neutral sulphate of the oxide of copper and red protoxide of copper.

It is probable that all other acids are capable of forming similar double salts with these two bases; but they cannot be so easily exhibited, because they are more soluble in alcohol.

If it were permitted to ground a general rule on a single example, I should conclude that, when an acid is supersaturated with two bases, both of them, taken together, contain the same quantity of oxygen as a single base must do, in order to form a subsalt with the acid; and that the oxygen of the one base must be a multiple of that of the other by 1, 2, 3...

2. Double Salts with two Acids, or Substances representing Acids, and one Base.

These salts have been little examined, and their number seems to be small. The only examples, in any degree well established, are afforded by the combinations of a base with sulphur and sulphuretted hydrogen, and with sulphur and sulphuric acid. It is probable, that in these cases the two [negative] substances divide the [positive] one between them, and take up either equal portions of it, or such portions as are in the proportion of 1 to 2, 3, or 4.

I have mentioned, in the First Continuation of my Essay, on occasion of the investigation of the relation of the oxygen of the acids to that of the bases of salts, a double salt consisting of the nitric and arsenic acids with protoxide of lead. When I endeavoured

voured to analyse this salt, I found its component parts indefinitely varying, accordingly as the solution from which it was crystallized was more or less concentrated. Since also it is decomposed by solution in water, it does not appear that it can be considered as a double salt: and it is perhaps only an intimate mixture of crystallized particles of the nitrate with those of the arseniate of the protoxide of lead.

Another similar instance has also occurred to me. I had mixed together a solution of muriate of ammonia and of muriate of the oxide of iron, and, having concentrated them, left them to crystallize. The salt which I obtained had formed cubes of a fine ruby colour; and upon analysing them, I found only $1\frac{3}{4}$ per cent. of the oxide of iron. When dissolved in water, they lost their colour, and I obtained from the solution first an almost colourless, and then a light reddish-yellow salt, which in some parts was free from any tinge of colour, and in others was unequally coloured, and only of an orange red. Consequently this triple combination is to be considered rather as a mixture, than as a true double salt.

[To be continued.]

XXXIII. *Observations on Electrical and Chemical Terms.* By
Mr. J. MURRAY.

Colchester, March 4, 1814.

SIRS,—I THANK you for your prompt insertion of my paper in No. 189 of the Philosophical Magazine and Journal. Be pleased to supply the word *except* before “on the latter supposition.” In reference to the question of *theoretic electricity*, I may further remark, that it is a solecism in philosophical language, as in logic, to use the term *negative electricity*. To charge a jar with *nothing*, (for the *negation* must mean here, as it does in common language, an *absolute privation*,) is incompatible with a correct mode of expression, and it happens that this *negation exhibits powers as active and positive as its antagonist*. We cannot attribute to a state of *rest*, the lively character of *motion*. If two powers be intimately blended together (rosin on sulphur and red lead), and projected by an elastic gum bottle against a figure described by *positive electricity*, on the ball connected with an electric sphere, *charged positively*, the *rosin* or *inflammable substance* will separate from the mass, and adhere to the *communicated electricity*; and if *negative electricity* is the agent employed, the *metallic oxide* will be the *subject of attraction*. These are experiments familiar to every electrician. In my opinion, the *same fluid* in *different quantities* should only attract *different portions* of the *same substance*.

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