

CXCIV.—*The Interaction of Metallic Sulphates and Caustic Alkalis.*

By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.

THE ultimate action of caustic alkalis on boiling solutions of sulphates of the heavy metals results, as is well known, in the precipitation of the metal as oxide or hydroxide, but it is only in a very few cases that any knowledge exists as to the product of the reaction at the ordinary temperature, although a basic sulphate is generally held to be formed, and many such basic sulphates have been isolated by various methods of procedure (see Habermann, *Monatsh.*, 1884, 5, 442; Gorgeu, *Compt. rend.*, 1882, 94, 1425; Pickering, *Trans.*, 1880, 37, 807; *Chem. News*, 1882, 45, 121, and 1883, 47, 181). For the purposes of an investigation to be described subsequently, it became necessary to ascertain the composition of these precipitates in the case of iron and copper, and the results thus obtained have been supplemented by an examination of the sulphates of other metals.

The examination was made by ascertaining the amount of alkali, generally either sodium or calcium hydroxide, required for the complete precipitation of the metal, and also the amount required to produce an alkaline reaction, using phenolphthalein as indicator.

The precipitates are all of a bulky and flocculent nature, and the completion of the precipitation cannot be ascertained by allowing them to settle, and then adding more of the alkali: filtration is necessary; and the method which had to be adopted was to add various quantities of the alkali to similar quantities of the sulphate, and ascertain by successive approximations the amount of alkali necessary to ensure complete precipitation. In some cases, of course, this can be ascertained by the use of a more delicate test than the addition of more alkali.

Weak solutions were used in all cases, their strength being about one gram-molecule in 100 litres.

The general character of the reaction appears to be similar with all the metallic sulphates examined, and with all the caustic alkalis. The metal is first precipitated as a basic sulphate of definite composition, which, on the addition of more alkali, is converted into a second, more highly basic sulphate, before any alkaline reaction becomes evident in the liquid. In some cases, the transformation takes place in two distinct stages.

In every instance examined, the products of the reaction, so far as the basicity of the precipitates is concerned, are the same, whether soda or lime be used, but the precipitates are not always identical in other respects, and this has been ascertained to be due to the fact that, when lime is used, they retain a considerable amount of the calcium sulphate formed in the reaction. The basicity of the products will, however, alone be discussed at present.

Copper Sulphate.

The basic sulphates of copper were investigated by the author in 1883 (*Chem. News*, **47**, 181), and it was ascertained that two such existed in definite form: $3\text{CuO}, \text{SO}_3$, obtained by boiling a solution of copper sulphate, and $4\text{CuO}, \text{SO}_3$, obtained (a) by precipitating copper sulphate solutions with an amount of potash not exceeding 0.75 equivalent; (b) by decomposing the sulphate with an acetate, or (c) by digesting copper hydroxide with a solution of the sulphate. These results were based on the analysis of the precipitates.

When an alkali is added gradually to a weak solution of copper sulphate, a point is reached when the liquid begins to show a slight alkaline reaction, but this reaction is temporary, and more alkali must be added before a permanent alkalinity is obtained. The gradual absorption of alkali after the first temporary alkalinity occurs extends over two or three days. The equivalents of alkali required to produce the initial and permanent alkaline reaction, together with the equivalents required to precipitate the copper completely, were found to be:

	Complete precipitation.	Initial alkalinity.	Permanent alkalinity.
BaO	—	0.903	0.903
CaO	0.752	{ 0.864 0.877	{ 0.910 0.910 0.904
Na ₂ O	0.766	{ 0.833 0.851	{ 0.904 0.897
Li ₂ O	—	0.808	0.903
K ₂ O	(0.75)	0.805	0.893
Mean	0.756	—	0.901

The precipitation of the metal is complete when the alkali reaches 0.75 equivalent, an amount showing that the basic sulphate then formed must have the formula $4\text{CuO},\text{SO}_3$ (the value inserted for potash is that given by the investigation of 1883). This sulphate is evidently converted into a more basic one by further addition of alkali, and permanent alkalinity is reached in all five cases when the amount added amounts to 0.9 equivalent. This represents the formation of $10\text{CuO},\text{SO}_3$. In only one instance, that of baryta, is the point of initial alkalinity identical with that of permanent alkalinity, an exception probably connected with the insolubility of barium sulphate. With lithia and potash, initial alkalinity occurs with 0.8 equivalent, but with soda and lime the values are higher. It seems most probable, however, that in all cases the point of initial alkalinity indicates the existence of a basic sulphate intermediate between the first and final products, although in some cases it may be impossible to obtain this intermediate compound unmixed with a certain amount of the final product, and hence the quantity of alkali absorbed is abnormally large. The initial alkalinity certainly marks a point at which there is a very great alteration in the rate at which the alkali disappears, an almost instantaneous absorption, changing to one of extreme slowness, although its rate varies with the alkali used. Moreover, the product obtained at the point of initial alkalinity is not intermediate in character between the highest and lowest sulphate, as it would be if it were a mixture of these two. Taking the case of lime: the first product, $4\text{CuO},\text{SO}_3$, is a light, opaque, blue or greenish-blue substance, which settles comparatively quickly in the liquid; the final product, $10\text{CuO},\text{SO}_3$, is of a darker, full blue colour, less opaque, and it settles much more slowly: but the intermediate product, obtained when about 0.8 equivalent is added, is almost as dark as the compound $10\text{CuO},\text{SO}_3$, and is even more voluminous, settling very slowly indeed in the liquid. To give an example: 1 gram of hydrated copper sulphate was precipitated by different amounts of lime-water, so as to give the three basic sulphates in question, the total volume of the liquid in each case being 171 c.c.: after one hour, the precipitates occupied 83, 145 and 136 c.c. respectively, the second sulphate evidently not being intermediate in properties between the first and the third. This was repeated many times, and always with the same result.

It is fairly certain, therefore, that in the case of the action of all the alkalis (except baryta) on copper sulphate, an intermediate compound is formed, and it is probable, from the results with lithia and potash, that its formula is $5\text{CuO},\text{SO}_3$, corresponding to the addition of 0.8 equivalent of alkali.

It is necessary to add the alkali very slowly and cautiously to the

sulphate in order to obtain the first compound, $4\text{CuO},\text{SO}_3$, pure; any local excess of alkali tends to form some of the more basic sulphates, and then, more than 0.75 equivalent will be required to complete the precipitation. In the same way, it requires great care to obtain the final sulphate, $10\text{CuO},\text{SO}_3$, without the production of any copper hydroxide in cases where such is produced by excess of alkali, as it is where soda, lithia or potash is used, the precipitate then turning black after a time. When precipitated with care, the basic sulphates themselves seem to be quite permanent in the liquids from which they are thrown down.

It was found that the final reaction with lime-water, that is, to permanent alkalinity, was practically constant throughout the range of ordinary atmospheric temperatures, but that at higher temperatures the precipitate became less basic, attaining at 100° almost to the composition of $4\text{CuO},\text{SO}_3$. The values obtained were:

At	5°, 0.916	CaO required.	10CuO,SO ₃ requires 0.9	CaO.
„	25°, 0.912	„	„	„
„	40°, 0.825	„	„	„
„	70°, 0.809	„	„	„
„	100°, 0.764	„	4CuO,SO ₃ requires 0.75	CaO.

The results obtained when excess of lime-water is added to copper sulphate are described in a subsequent communication (p. 1995).

Iron Sulphates.

With ferrous sulphate, the precipitation of the whole of the iron is coincident with the first appearance of an alkaline reaction, and, although duplicate determinations were not very concordant, the complete precipitation evidently occurs when a basic sulphate of the formula $10\text{FeO},\text{SO}_3$ is formed, analogous to the final product in the case of copper sulphate. The values obtained were:

	With Soda.	With Lime.
	0.930 equiv.	0.868 equiv.
	0.887 „	0.892 „
	0.884 „	0.881 „
	0.914 „	0.874 „
Mean	0.904 „	0.879 „

The temporary alkalinity disappears, and more alkali must be added before it becomes permanent, but the rate at which it disappears is even less than in the case of copper sulphate, and the reaction is not complete for many days. It is difficult therefore to determine the point of completion with any degree of accuracy, but it evidently corresponds with the removal of all the SO_3 from the basic sulphate; the mean

of three determinations with soda gave 1.029 Na_2O as having been used, and five determinations with lime gave 1.013 CaO .

With ferric sulphate, the complete precipitation of the metal and the first appearance of alkalinity were coincident, the equivalents of alkali required being 3×0.772 in the case of soda, and 3×0.817 (mean of 0.830 and 0.803) in the case of lime. The further absorption of alkali occurs as in other cases, but with such slowness that it is almost impossible to determine the final point: using soda, this point appeared to be 3×0.860 equivalents. None of these values is sufficiently concordant or exact to justify the assigning of any formula to the basic sulphates formed; all that is certain is that a basic sulphate is formed, and that it is then converted by further alkali into a more highly basic one.

An investigation of the basic ferric sulphates was published by the author in 1880 (Trans., 1880, 37, 807); the investigation was on lines different from those followed here, and, of the many basic sulphates supposed to exist, evidence in favour of one only was found, namely, $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$; this sulphate would correspond with a reaction requiring the addition of 3×0.833 equivalents of alkali; the determinations just quoted give values neighbouring on this quantity, and, no doubt, this basic sulphate figures in the precipitation of ferric sulphate by alkalis.

Nickel Sulphate.

With soda, the whole of the metal was precipitated when the alkali amounted to 0.422 equivalent, and the liquid then showed a barely perceptible alkaline reaction. With lime-water, a similar result was obtained, the value found being 0.404 equivalent. This indicates the formation of $5\text{NiO} \cdot 3\text{SO}_3$. When more of either of these alkalis was added, no further increase in alkalinity occurred until the total added amounted to either 0.6 or 0.8 of an equivalent. Whether the one or the other of these two proportions marks the point at which a definite increase in the pink colour of the phenolphthalein is noticed seems to depend somewhat on the conditions under which the reaction occurs, such as the dilution of the liquid, and the rate at which the alkali is added. Both stages may sometimes be noticed in the same experiment, if the bulk of substance dealt with, and the conditions facilitating the observation of changes of colour, are suitable.

The values obtained on various occasions were:

With soda	0.598	With soda	0.812
„ lime	0.582	„ lime	0.803
„ „	0.596	„ „	0.810
Mean	0.592		0.808

These indicate the existence of $5\text{NiO}, 2\text{SO}_3$ and $5\text{NiO}, \text{SO}_3$, both of which are, no doubt, formed in succession from the primary product, $5\text{NiO}, 3\text{SO}_3$. The last change, to $5\text{NiO}, \text{SO}_3$, is the one which is most marked.

Cobalt Sulphate.

With cobalt sulphate, the results are different from those with nickel sulphate, for a permanent alkaline reaction appears as soon as the precipitation of the metal is complete. This occurs where the soda amounts to 0.759 equivalent, or three-quarters of that necessary for total decomposition, representing therefore the formation of $4\text{CoO}, \text{SO}_3$.

There is, apparently, a preliminary action in the case of cobalt, as in the case of the other sulphates. A faint alkaline reaction first appears when the alkali added amounts to about 0.3 equivalent, but further additions of alkali cause no corresponding increase of alkalinity until, as has been said, the amount added reaches 0.75 equivalent. This preliminary stage, however, does not serve to indicate the composition of the basic sulphate present, as part of the metal is still in solution.

The precipitate formed during this first stage is green, but when more alkali is added it becomes blue.

Manganese Sulphate.

The whole of the metal in this case was not precipitated by soda until the latter amounted to 1.019 equivalents. There is here, therefore, no indication of any basic sulphate being formed. The reaction with lime was not examined.

Zinc Sulphate.

With zinc sulphate and soda, the complete precipitation of the metal was coincident with the appearance of a permanent alkaline reaction, and no preliminary or secondary reaction was noticed. The alkali required was found to be 0.795 equivalent, indicating, therefore, the composition of the precipitate to be $5\text{ZnO}, \text{SO}_3$.

Cadmium Sulphate.

With cadmium sulphate a slight pink colour was noticed (phenolphthalein being present) on the addition of only a small amount of soda, but it is the precipitate, and not the liquid, that becomes coloured; the latter shows no alkaline reaction until the whole of the

metal is precipitated. This occurs when the alkali amounts to 0.731 equivalent, indicating, although not very exactly, the formation of a sulphate of the composition $4\text{CdO},\text{SO}_3$.

Magnesium Sulphate.

With magnesium sulphate, soda completed the precipitation when it amounted to 1.034 equivalents. No basic sulphate therefore seems to be formed in this case.

Aluminium Sulphate.

The addition of soda to aluminium sulphate completes the precipitation when the quantity added reaches 3×0.611 equivalents, which implies that the basic sulphate formed is $5\text{Al}_2\text{O}_3, 6\text{SO}_3$. The slight excess in the soda over that calculated is accounted for by a further change, similar to that observed in other cases, since the precipitate is converted into a more basic sulphate by a further addition of alkali, the alkaline reaction not becoming permanent until the total alkali amounts to 3×0.95 molecules. With lime-water, a similar determination gave 3×0.970 molecules as requisite. The secondary action was a very slow one, requiring several days, and, possibly, was not quite complete even then, so that in all probability the final product is alumina containing no SO_3 .

As many as nine basic sulphates of aluminium have been stated by various chemists to have been obtained: but an examination undertaken by the present author in 1882 (*Chem. News*, **45**, 121) threw considerable doubt on the existence of all of them as definite compounds. The list of these did not contain the one now indicated.

Summary.

Alkalis added to solutions of the metallic sulphates here examined precipitate a definite basic sulphate, except in the case of manganese and magnesium, where the hydroxide is precipitated. After the precipitation is complete, the further addition of alkali converts the basic sulphate, either into another, sometimes consecutively into two other, more basic products (for example, copper, nickel), or into the hydroxide (aluminium). When one of the stronger alkalis (potash, soda) is added in excess, the product is probably always the hydroxide, but, in the case of lime, this does not appear to be so, at any rate not with the sulphates of copper and nickel, as will be shown in the following communication. In every case examined, different alkalis have given the same results as regards the basicity of the sulphates precipitated by them in each particular case. The existence of the following eleven

1988 PICKERING : THE CHEMISTRY OF BORDEAUX MIXTURE.

basic sulphates has been established in this way : the predominance of five as the coefficient of equivalents of metallic oxide present is very noticeable. Those marked with an asterisk are the ones formed when the whole of the metal has been precipitated from the solution, the others are products of the action of further quantities of alkali :

$5\text{NiO}, 3\text{SO}_3^*$, $5\text{NiO}, 2\text{SO}_3$, $5\text{Al}_2\text{O}_3, 3 \times 2\text{SO}_3^*$, $4\text{CuO}, \text{SO}_3^*$, $4\text{CoO}, \text{SO}_3^*$, $4\text{CdO}, \text{SO}_3^*$, $5\text{CuO}, \text{SO}_3$, $5\text{NiO}, \text{SO}_3$, $5\text{ZnO}, \text{SO}_3^*$, $10\text{CuO}, \text{SO}_3$, $10\text{FeO}, \text{SO}_3^*$.

The basic sulphates obtained by Habermann (*loc. cit.*), chiefly by adding ammonia to boiling solutions of the sulphates, differ in every case from the above, the compounds described by him being $7\text{CuO}, 2\text{SO}_3$, $7\text{NiO}, \text{SO}_3$, $5\text{CoO}, \text{SO}_3$, $4\text{ZnO}, \text{SO}_3$, and $2\text{CdO}, \text{SO}_3$. Gorgeu also obtained $3\text{MnO}, 2\text{SO}_3$, and Schindler, $2\text{ZnO}, \text{SO}_3$; the literature of the basic sulphates of copper, iron and aluminium will be found in the communications by the present author referred to above.
