CXCV.—*The Chemistry of Bordeaux Mixture.*

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BORDEAUX mixture, or *bouillie bordelaise,* has been in use as a fungicide since 1883. The discovery of its value was accidental. It had been the practice in the vineyards in the neighbourhood of Bordeaux to sprinkle those vines which were near a road with verdigris, in order to give them the appearance of having been poisoned, and so to prevent depredations. A mixture of lime and copper sulphate was soon substituted for the verdigris, being cheaper, and, when the downey mildew of America (*Peronospora viticola*) made its appearance in Europe, it was noticed (1882) that those vines which had received the copper dressing were those which kept their leaves longest, and were least affected by the disease.

The mixture in general use at present is made by adding 1·1 parts by weight of lime, made into a milk, to 1·6 parts of crystallised copper sulphate dissolved in 100 parts of water. This is known in America as the "normal" or "1·6" mixture. Occasionally, stronger or weaker mixtures are used, and sometimes the proportion of lime added is increased so as to be equal to that of the copper sulphate. For complete decomposition, the crystallised sulphate would require one-fifth of its weight of pure lime; therefore, the lime used in practice is always in considerable excess, even when a liberal allowance is made for impurities in it.

It is somewhat remarkable that the nature of the substance con-

stituting this mixture has not yet been elucidated. The reaction occurring is generally represented as resulting in the formation of copper hydroxide, although occasionally it is suggested that a basic sulphate may be formed, and an equation is given representing a basic sulphate ($2CuO,SO_3$) which, so far as is known, has no existence. That copper hydroxide is the product of the reaction scarcely admits of serious consideration, for this hydroxide, as is well known, loses its water and its blue colour in a very short time, turning black, whereas Bordeaux mixture remains quite blue for an indefinite period. It is true that caustic potash in excess of that required to form basic sulphate of copper results in the formation of some copper hydroxide, and that in Bordeaux mixture the alkali is in considerable excess; but it does not by any means follow that excess of lime will behave in the same manner as excess of potash.

That the action of lime on copper sulphate is somewhat variable and complicated would appear to be probable from the considerable variations which are noticed in the blue colour of the precipitate constituting Bordeaux mixture. These variations may sometimes be explained by differences in the colour of the lime used, but they are also due, as will be seen, to the fact that there are formed, under various conditions, substances with considerable differences of coloration. Occasionally the precipitate will be found to be violet, inclining even to purple: this coloration is probably accidental, and due to the presence of some pink compound formed by organic substances exhibiting the biuret reaction. On several occasions when dealing with emulsions of petroleum with basic copper sulphate, streaks of a pink compound have been noticed in the blue emulsion.

In Bordeaux mixture made with milk of lime, there must be free lime, and, generally, calcium carbonate, mechanically mixed with the precipitate, and any direct investigation of the composition of this precipitate would be of little value. Lime-water, therefore, was used instead of milk of lime; but, even then, any analysis of the precipitate was practically impossible, for it is very bulky and difficult to wash, whilst water, as will be shown, partly decomposes it, as also does carbon dioxide. The method of examination adopted, therefore, was to mix known weights of copper sulphate and lime in solution, and to deduce the composition of the precipitate formed by determining what was left dissolved in the liquid. This is either calcium sulphate only, or calcium sulphate and hydroxide where an excess of lime has been used; the latter was determined by titration, and the former, either as barium sulphate, or by evaporation to dryness and igniting. In some cases, the precipitation was effected in the presence of excess of sodium sulphate,

and then the mixed sulphates left in solution had to be discriminated by a separate determination of the amount of calcium in them.

As has been shown in the previous communication (p. 1983), the precipitation of the copper is complete when enough lime is added to form the basic sulphate $4CuO,SO_3$, and this sulphate is decomposed on further addition of alkali until the compound $10CuO,SO_3$ is formed; in addition to these, a sulphate of an intermediate composition, probably $5CuO,SO_3$, is also produced.

Although, as regards basicity, the precipitates formed when different alkalis are used are identical, a qualitative examination is sufficient to show that they are not identical in other respects. Thus, on precipitating copper sulphate with sufficient alkali to form $5CuO,SO_3$, the volume of the liquids being the same, the precipitate with lime is found to be of a pale blue, whereas that with soda is very much darker; the former, also, is either finer-grained or less dense than the latter, for, even after being allowed twenty-four hours to settle, it occupies a volume half as great again as the latter. The precipitate given by lithia resembles that with lime, and is even paler in colour and more bulky, whereas that given by potash resembles the soda precipitate, except that it is slightly darker. Similar differences in appearance are noticed if the precipitates consisting of $4CuO,SO_3$, obtained by different alkalis, are compared. The more minute state of division of the lime precipitates, as contrasted with those given by soda, is further illustrated by the greater emulsifying powers of the former, which will be described in a subsequent communication.    With the basic ferrous sulphates, it may be mentioned, a like difference of behaviour characterises the precipitates thrown down by different alkalis.

These differences, however, are not of a physical character only, for the two precipitates behave differently when treated with excess of the same alkali; the soda precipitate, when treated with a further equivalent of caustic potash, begins to blacken in half an hour; with a further equivalent of soda it begins to blacken in two hours; and with an equivalent of lime, blackening commences only after about six weeks: with the lime precipitate, however, blackening is produced by excess of soda only after two or three weeks, whereas excess of neither potash nor lime seem to have any effect on it.

Passing to the quantitative examination, Table I contains the values given when copper sulphate is precipitated with varying proportions of lime.    The molecular proportions of the reagents taken are entered in the first two columns, and the molecular composition of the precipitate, as given by the analysis of the residual solution, in the third.    The solution of copper sulphate taken

TABLE I.—*Precipitation of Copper Sulphate by Lime-Water.*

Proportions taken.

| | $CuSO_4$. | CaO. | Composition of precipitate. | |
|---|---|---|---|---|
| (1)...... | 10 | 7·5 | $10CuO,2·5SO_3,0·2\ CaSO_4$ | |
| (2)...... | 10 | 8 | $10CuO,\ 2SO_3,0·78CaSO_4$ | ⎱ |
| (3)...... | 10 | 8 | $10CuO,\ 2SO_3,0·46CaSO_4$ | ⎰ |
| (4)...... | 10 | 9 | $10CuO,\ SO_3,1·45CaSO_4$ | ⎱ |
| (5)..... | 10 | 9 | $10CuO,\ SO_3,1·34CaSO_4$ | ⎰ |
| (6)..... | 10 | 9 | $10CuO,\ SO_3,1·25CaSO_4$ | ⎰ |
| (7)...... | 10 | 18 | $10CuO,SO_3,1·12CaSO_4,2·66CaO$ | ⎱ |
| (8) ..... | 10 | 18 | $10CuO,SO_3,0·88CaSO_4,3·00CaO$ | ⎰ |
| (9)...... | 10 | 27 | $10CuO,SO_3,1·11CaSO_4,3·05CaO$ | ⎱ |
| (10)...... | 10 | 27 | $10CuO,SO_3,1·11CaSO_4,2·73CaO$ | ⎰ |
| (11)...... | 10 | 36 | $10CuO,SO_3,0·84CaSO_4,3·11CaO$ | |
| | | *Mean* ........ | $10CuO,SO_3,1·01CaSO_4,2·91CaO$ | |
| (12)...... | 10 | 54 | $10CuO,SO_3,1·38CaSO_4,4·44CaO$ | |
| (13)...... | 10 | 108 | $10CuO,SO_3,0·98CaSO_4,7·24CaO$ | |
| (14)...... | 10 | 180 | $10CuO,0·47SO_3$ | 15·7CaO |
| (15)...... | 10 | 240 | $10CuO,$ | 18·6CaO |
| (16)...... | 10 | 300 | $10CuO,$ | 20·6CaO |
| (17)...... | 10 | 490 | $10CuO,$ | 28·1CaO |
| (18)...... | 10 | 1020 | $10CuO,$ | 32·6CaO |
| (19)...... | 10 | 1840 | $10CuO,$ | 28·5CaO |
| (20)...... | 10 | 5100 | $10CuO,$ | 31·4CaO |
| | | *Mean* ........ | $10CuO,$ | 30·1CaO |

contained 10 per cent. of $CuSO_4,5H_2O$, and the lime-water contained about 0·135 per cent. of CaO ; in the case where the smallest proportion of lime-water was used, the mixture would be of about half the strength of normal Bordeaux mixture. The proportions in the table are all expressed so as to refer to 10CuO.

In the first six experiments, the lime added was only just sufficient to form one or other of the three definite basic sulphates, but in all three cases, as will be seen, these contain a certain amount of calcium sulphate. With $4CuO,SO_3$ (No. 1), the amount is very small, with $5CuO,SO_3$ (Nos. 2 and 3) it is much greater (although it varies considerably in the duplicate determinations), and with $10CuO,SO_3$ (Nos. 4–6) it is greater still, there being then more $SO_3$ present as calcium sulphate than in the basic copper sulphate itself. Taking into consideration the large and approximately constant proportion of calcium sulphate in the latter case, and the fact that the amount here present is very different from what it is with the less basic sulphates, the conclusion is that the calcium sulphate must be present as a chemical constituent of the molecule itself. The values, however, are not sufficiently near to a simple proportion to lead to a definite formula for the complex sulphate.

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No doubt, all these precipitates are unstable compounds, the composition of which would be affected by such circumstances as the temperature and strength of the solution; indeed, they readily give up some of their calcium sulphate to water. This was established as follows: the mixture in No. 6 was filtered, and the filtrate measured and analysed; the measurement showed what volume of liquid was retained by the precipitate on the filter; the precipitate with this liquid was then mixed with water equal in volume to that originally present, and the amount of sulphate passing into solution was determined. This was found to be greater than that in the liquid adhering to the precipitate, so that some of the sulphate must have been derived from the precipitate itself. The precipitate, which originally contained $1.25CaSO_4$, contained now only $1.01CaSO_4$. A similar experiment with the less basic precipitate in No. 3 gave similar results, the $0.46CaSO_4$ originally present being reduced to $0.35CaSO_4$.

The circumstances conditioning the amount of calcium sulphate in these basic sulphates were examined in other experiments, which may be described before dealing with the further results given in Table I.

Table II contains results in which the precipitation was effected in the presence of excess of calcium sulphate. In Nos. 23, 21, 26, 27 and 24 the calcium sulphate added was equivalent to one, two,

TABLE II.—*Precipitation of Copper Sulphate by Lime-Water with Excess of Calcium Sulphate Present.*

| | Proportions taken. | | | |
|---|---|---|---|---|
| | $CuSO_4$. | CaO. | $CaSO_4$. | Composition of precipitate. |
| | (a). | $4CuO,SO_3$ formed. | | |
| (1) ............... | 10 | 7·5 | 0 | $10CuO,2·5SO_3,0·2CaSO_4$ |
| (21) ............ ... | 10 | 7·5 | 15 | $10CuO,2·5SO_3,$ (no $CaSO_4$) |
| (22) ............... | 10 | 7·5 | Saturated | $10CuO,2·5SO_3,0·27CaSO_4$ |
| | (b). | $5CuO,SO_3$ formed. | | |
| (2) (3) ......... | 10 | 8 | 0 | $10CuO,2SO_3,0·62CaSO_4$ |
| (23) ............... | 10 | 8 | 8 | $10CuO,2SO_3,0·14CaSO_4$ |
| (24) ............... | 10 | 8 | 24 | $10CuO,2SO_3,0·20CaSO_4$ |
| (25) ............... | 10 | 8 | Saturated | $10CuO,2SO_3,0·78CaSO_4$ |
| | (c). | $10CuO,SO_3$ formed. | | |
| (4) (5) (6) ...... | 10 | 9 | 0 | $10CuO,SO_3,1·35CaSO_4$ |
| (26) ............... | 10 | 9 | 18 | $10CuO,SO_3,1·43CaSO_4$ ⎱ |
| (27) ............... | 10 | 9 | 18 | $10CuO,SO_3,1·03CaSO_4$ ⎰ |
| (28) ............... | 10 | 9 | Saturated | $10CuO,SO_3,1·15CaSO_4$ |

two, two and three times respectively, that formed in the reaction, excess of lime-water neutralised with sulphuric acid being added

for the purpose; but the water present was increased in similar proportion, so that the strength of the solution as regards its calcium sulphate contents was the same in all cases. All these solutions, however, were supersaturated with calcium sulphate, for 100 parts of water at 15° dissolve 0·129 gram of lime, but only 0·197 gram of calcium sulphate (equivalent to 0·081 gram CaO), so that the amount available for combining with the basic sulphate would be increased by increasing the amount of calcium sulphate solution present, yet no such increase of sulphate in the precipitate is produced thereby.

The supersaturated solution of calcium sulphate obtained by neutralising lime-water with sulphuric acid remains very persistently supersaturated, and no trace of sulphate is deposited for at least forty-eight hours; it is improbable therefore that these precipitates were contaminated with calcium sulphate which had crystallised out, as they were all filtered from the liquid within twenty-four hours of being precipitated. To obviate such a possibility, however, the experiments were repeated in the presence of a large weighed crystal of selenite, on to which any calcium sulphate would be deposited from the liquid, whilst, at the same time, the liquid would be kept saturated. The mixtures were left for nine weeks before analysis (which included the determination of the increase in weight of the selenite crystals); the results (Nos. 22, 25 and 28) give substantially the same values as the other experiments for the composition of the precipitates. It should be mentioned, however, that one series made at a lower temperature gave higher values in the case of all three basic sulphates for the amount of calcium sulphate present; this series has not been included here, as there was another circumstance connected with it which prevented its being strictly comparable with the others.

Of the three basic sulphates, $10CuO,SO_3$ is the one in which the calcium sulphate contents show least variation. The mean of the various determinations gives the approximate formula for this compound as $10CuO,SO_3,1·28CaSO_4$; the means for the other basic sulphates are $10CuO,2SO_3,0·47CaSO_4$ and $10CuO,2·5SO_3,0·16CaSO_4$.

For reasons connected with an investigation which will be described later, it was necessary to ascertain whether the composition of these basic copper sulphates was modified by the presence of excess of sodium sulphate in the solution. With this object in view, known quantities of sodium sulphate were added to the copper sulphate before the addition of the lime. The results are given in Table III. With the basic sulphate $4CuO,SO_3$, the small amount of calcium sulphate present in it is entirely ousted, and its place

TABLE III.—*Precipitation of Copper Sulphate by Lime-Water with Sodium Sulphate Present.*

| | Proportions taken. | |
| | $CuSO_4$. | CaO. | $Na_2SO_4$. | Composition of precipitate. |
|---|---|---|---|---|
| | | (*a*). | $4CuO,SO_3$ formed. | |
| (1)............ | 10 | 7·5 | 0 | $10CuO,2·5\ SO_3,0·2\ CaSO_4$ |
| (29)............ | 10 | 7·5 | 30 | $10CuO,2·55SO_3,0·75Na_2SO_4$ |
| | | (*b*). | $5CuO,SO_3$ formed. | |
| (2) (3) ...... | 10 | 8 | 0 | $10CuO,\quad 2SO_3,0·62CaSO_3$ |
| (30)............ | 10 | 8 | 30 | $10CuO,2·02SO_3,0·34CaSO_4,0·83Na_2SO_4$ |
| | | (*c*). | $10CuO,SO_3$ formed. | |
| 4) (5) (6)... | 10 | 9 | 0 | $10CuO,\quad SO_3,1·35CaSO_4$ |
| (31)............ | 10 | 9 | 15 | $10CuO,1·05SO_3,1·03CaSO_4,0·9\ Na_2SO_4$ |
| (32)............ | 10 | 9 | 30 | $10CuO,1·09SO_3,1·21CaSO_4,0·82Na_2SO_4$ |
| (33)............ | 10 | 9 | 45 | $10CuO,1·01SO_3,0·99CaSO_4,1·41Na_2SO_4$ |
| (34)............ | 10 | 9 | 45 | $10CuO,1·02SO_3,0·77CaSO_4,1·27Na_2SO_4$ |
| *Mean of 24 to 27* ......... | | | | $10CuO,1·04SO_3,1·00CaSO_4,1·10Na_2SO_4$ |

is taken by a proportionately large amount of sodium sulphate. A similar change occurs with both the other basic sulphates, although the displacement of the calcium sulphate is not complete; with $5CuO,SO_3$ about half the calcium sulphate is removed, and with $10CuO,SO_3$ about two-thirds; whilst in all cases the amount of sodium sulphate in the precipitate is greater than that of the calcium sulphate which it displaces.

The four determinations with the most basic sulphate clearly indicate a definiteness in composition, for the sum of molecular proportions of sodium and calcium sulphates present is constant, in spite of the variations in the proportions of sodium sulphate taken, and the precipitate is representable by the formula

$$10CuO,SO_3,2(Na_2,Ca)SO_4.$$
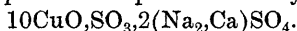
In only one of the determinations (33) are the values at all at variance with this formula, but the experimental errors are considerable, for the amount of $SO_3$ in the precipitate is determined from the difference between quantities of ten to twenty times its magnitude, and the lime to be determined is present in very small amount. It is probable, indeed, that the molecular proportions of calcium and sodium sulphate are constant throughout, instead of being merely interchangeable, and the mean of the results, as will be seen, gives almost exactly equal molecular proportions of these two.

It will be noticed that the $SO_3$ united with the copper oxide is not, in these cases, represented by an exact number of equivalents; this

is because the values given are dependent on the analysis, being the difference between the total $SO_3$ in the precipitate and that united with the lime and soda present, instead of being deduced, as in other cases, from the amount of lime-water neutralised.

With the two less basic sulphates, the experiments were not extended so as to determine the exact formula of the precipitates ; it is noticeable, however, that with the second sulphate the formula approximates to $10CuO,2SO_3,(Na_2,Ca)SO_4$, that is, a compound containing only half as much of the neutral sulphates as is present in the most basic sulphate. In all three cases the proportion of total $SO_3$ to CuO in the molecule seems to be nearly constant, and approximates 3 : 10 ; the less there is present in combination with the copper the more there is present as sulphate of calcium or sodium.

Reverting now to Table I, the experiments in the lower portion of it refer to cases where lime is added in excess. The results are somewhat remarkable. With all proportions of lime between 10 and 40 CaO to each 10CuO (Nos. 7 to 11) the same compound is formed, this being the basic copper sulphate combined with one molecule of calcium sulphate and three of calcium oxide, or, in other words, a double basic sulphate of copper and calcium of the formula $10CuO,SO_3,4CaO,SO_3$. When the proportion of lime taken is increased beyond 40CaO to each 10CuO, the precipitate rapidly becomes more basic, and with proportions exceeding 100CaO the $SO_3$ in it begins to disappear, until, with still greater excess of lime, we get a precipitate which is a double oxide of copper and calcium. This attains to a constant composition when the proportion of lime reaches about 500CaO to 10CuO, and remains so up to the end of the series, where 5100CaO to 10CuO was taken. The composition of this double oxide is $CuO,3CaO$ ; the mean of the last four determinations giving $CuO,3{\cdot}01CaO$.

Between the double oxide and the double basic sulphate

$$10CuO,SO_3,4CaO,SO_3,$$
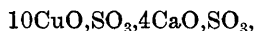
there is probably another definite compound formed, and, as the lower basic sulphates of calcium and of copper appear to be analogous $(4M''O,SO_3)$, we may conjecture that the higher ones are so also, and that the highest double basic sulphate has the formula $10CuO,SO_3,10CaO,SO_3$. The values found in No. 13 are very close to this, being $10CuO,SO_3,8{\cdot}2CaO,SO_3$, but it would require several determinations with amounts of lime intermediate between those in Nos. 13 and 14 to settle whether the limit here suggested is really reached before the $SO_3$ begins to be abstracted from the molecule.

The existence of this second double basic sulphate is emphasised

when the results are plotted out. Plotting the lime in the pre-
cipitate against the amount of lime taken (it is best to take the
logarithms of these quantities), it is clear that the values, when
the precipitates contain $CaSO_4$, are not continuous with those when
they contain none; the experiments 11 to 13 lie on one straight
line, and 14 to 17 on another, there being some considerable change
between 13 and 14. The rest of the figure is made up of three
horizontal lines, the first representing the results of Nos. 1 to 6,
where there is no lime in the precipitate, and the second represent-
ing the results of Nos. 7 to 11, where the double basic sulphate is
formed, and the third, the results of Nos. 17 to 20, when the double
oxide has attained constancy of composition.

In Bordeaux mixture, the highest proportion of lime generally
used is five equivalents to each equivalent of copper sulphate, that
is, equal weights of the two; this is about the proportion in experi-
ment 12 in Table I, but, as the lime is always far from pure, the
actual proportions of calcium oxide would be smaller, and the
reaction occurring would rarely go beyond the stage reached in
experiments 7 to 11, that is, $10CuO,SO_3,4CaO,SO_3$ would be the com-
compound formed. With still smaller proportions of lime, or with
impure and carbonated lime, we should get the compound

$$10CuO,SO_3,1\cdot3CaSO_4,$$
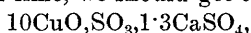
or even a less basic sulphate down to $4CuO,SO_3$. The different
appearance of these products would account for the differences
observed in the appearance of Bordeaux mixture, the basic sul-
phates, $4CuO,SO_4$ and $10CuO,SO_3,4CaO,SO_3$, being much paler in
colour than the intermediate sulphates.

When Bordeaux mixture is applied to trees, it liberates, after a
time, small quantities of copper sulphate, and it is to this soluble
copper that its fungicidal action is attributable. The reaction, no
doubt, consists of $xCuO,ySO_3 + (x-y)CO_2 = (x-y)CuCO_3 + yCuSO_4$.

One of the disadvantages attending its use, however, is that a
certain time elapses before the fungicidal action comes into play.
The nature of the compound of which Bordeaux mixture has now
been found to consist, will explain the occurrence of this delay, for,
with a basic sulphate of copper and calcium, the basic sulphate of
copper would probably not be attacked by the carbon dioxide until
all the basic sulphate of calcium in it had been decomposed. That
this is the case was verified by suspending in equal bulks of water
various basic sulphates containing the same amount of copper,
passing the same slow stream of carbon dioxide through the liquids,
and testing these at intervals to ascertain how long it took before
recognisable quantities of copper passed into solution. The results
were as follows:—

| | | |
|---|---|---|
| With $10CuO,2·5SO_3,0·16CaSO_4$ ............... | 3—5 minutes | |
| ,,    $10CuO,2SO_3,0·47CaSO_4$ ................. | 10 | ,, |
| ,,    $10CuO,SO_3,1·28CaSO_4$ ................. | 10 | ,, |
| ,,    $10CuO,SO_3,4CaO,SO_3$ .................... | 45 | ,, |

The length of the interval in the case of the last compound, as compared with that in the case of the others, is very noticeable. Excess of lime had, of course, to be added to precipitate the last sulphate, but that was removed by filtration before the precipitate was treated with the carbon dioxide; when it was not removed (and this is the case with Bordeaux mixture in practice) a still longer interval, namely, seventy-five minutes, elapsed before copper was liberated. The longer interval in the case of the second and third sulphate, as compared with the first, is, of course, due to the smaller amounts of copper sulphate which they are able to liberate.

The delay in the action of the fungicide would, therefore, be obviated by using only sufficient lime to produce the basic sulphate $4CuO,SO_3$, instead of the double basic sulphate $10CuO,SO_3,4CaO,SO_3$; there would also be a considerable economical advantage in doing so, for the fungicidal value depends on the amount of normal copper sulphate eventually liberated, and the basic sulphate $4CuO,SO_3$ will liberate two and a half times as much of the normal sulphate as will $10CuO,SO_3$, calculated on the same weights of copper sulphate used in preparing them. If, on the other hand, the proportion of lime used were increased to about five times that of the copper sulphate (actual weights), the insecticidal value would be entirely destroyed, for the product then would consist of the double oxide, without any $SO_3$ in it.

To make the basic sulphate $4CuO,SO_3$, it is necessary to use lime-water instead of milk of lime, and this would be a further advantage from several other points of view, for the presence of solid lime clogs and wears the spraying nozzles, and entails loss of material, owing to its being easily knocked off the leaves.

One part by weight of crystallised copper sulphate requires about 134 c.c. of lime-water for its precipitation (the completion of which should, of course, always be verified by testing with ferrocyanide) ;* any increase in the proportion of lime would result in a diminution of the fungicidal value; thus, an increase to 143 c.c. would result in the precipitation of $10CuO,2SO_3,xCaSO_4$, and a consequent reduction of the efficacy by one-fifth.

A Bordeaux mixture made as here suggested would be rather more efficacious than the "normal" mixture, although it would contain less than half the amount of copper, and would also cost less

* A solution containing 0·002 per cent. of $CuSO_4,5H_2O$ gives a visible coloration with ferrocyanide.

than half.  Of course, the volume of lime-water required would vary somewhat with the temperature, but the variation in solubility of lime throughout the range of ordinary atmospheric temperatures is small, being given as 0·137 part in 100 parts of water at 5°, and 0·125 part at 20°.  According to these values, 135 c.c. would be required at 5°, and 123 c.c. at 20°, to precipitate the copper in one gram of $CuSO_4,5H_2O$.  The former agrees almost exactly with the amount (134 c.c.) which has been found necessary in practice when working either at winter or summer temperatures.

A few experiments were made using caustic soda (free from carbonate) instead of lime-water.  The results are given in Table IV.

TABLE IV.—*Precipitation of Copper Sulphate by Caustic Soda.*

| | | Proportions taken. | | |
|---|---|---|---|---|
| | $CuSO_4$. | $Na_2O$. | $Na_2SO_4$. | Composition of precipitate. |
| (35)  ......... | 10 | 7·5 | — | $10CuO,2·5SO_3,(0·01Na_2SO_4)$ |
| (36)  ......... | 10 | 8 | — | $10CuO,  2SO_3,$ (no $Na_2SO_4$) |
| (37)  ......... | 10 | 9 | — | $10CuO,   SO_3, 0·06Na_2SO_4$ |
| (38)  ......... | 10 | 9 | 15 | $10CuO,   SO_3, 0·5  Na_2SO_4$ |
| (39)  ......... | 10 | 9 | 45 | $10CuO,   SO_3, 1·33Na_2SO_4$ |

When the basic sulphates formed are $4CuO,SO_3$, or $5CuO,SO_3$, there is no sodium sulphate combined with them, and where $10CuO,SO_3$ is the product, the amount is so small that it is almost within the limits of experimental error, namely, $0·06Na_2SO_4$.  When an ,excess of sodium sulphate is present, however, the amount in the precipitate is increased, but the experiments were not extended far enough to show what ultimate limits are attained.    The absence of any sodium sulphate in the precipitate consisting of the less basic sulphates is in harmony with a similar observation made in 1883 (*Chem. News*, **47**, 182) as regards $4CuO,SO_3$ when precipitated by potash.

The differences in the appearance and behaviour of the basic sulphates of copper when they are precipitated by lime or soda is fully explained by these results (see p. 1990), for identical substances are not formed in the two cases, although the proportions of $CuO:SO_3$ are the same.
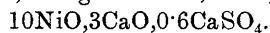
The behaviour of different alkalis towards other metallic sulphates indicates differences similar to those observed in the case of copper sulphate.  This is evidently so with ferrous sulphate, the precipitate formed by lime being different in colour and much more bulky, when compared with that formed by soda, although with both alkalis the basicity is the same, $10M''O,SO_3$ (p. 1984). Ferrous sulphate, however, is not a convenient salt for investiga-

tion, owing to its absorption of oxygen, and a few experiments were made with nickel sulphate instead.

TABLE V.—*Precipitation of Nickel Sulphate by Lime-Water.*

Proportions taken.

| | $NiSO_4$. | CaO. | $Na_2SO_4$. | Composition of precipitate. |
|---|---|---|---|---|
| (40) ............ | 10 | 8 | — | $10NiO, \quad 2SO_3, 0.11CaSO_4$ |
| (41) ............ | 10 | 24 | — | $10NiO, 0.34SO_3, 2.48CaO$ |
| (42) ............ | 10 | 48 | — | $10NiO, 0.49SO_3, 3.64CaO$ |
| (40) ............ | 10 | 8 | 0 | $10NiO, \quad 2SO_3, 0.11CuSO_4$ |
| (43) ............ | 10 | 8 | 17 | $10NiO, 1.74SO_3, 0.16CaSO_4$ |
| (44) ............ | 10 | 8 | 52 | $10NiO, 1.91SO_3, 0.64CaSO_4$ |

The results are given in Table V. The most basic sulphate of nickel had been found to be $5NiO, SO_3$ (see p. 1985), and this sulphate alone was examined. As seen from No. 40, it, like the corresponding copper compound (Nos. 2 and 3, Table I), contains some calcium sulphate, but in quantity so small that it might almost be attributed to experimental error. On raising the amount of lime used beyond that required for the formation of the basic sulphate, we get, unlike the case of copper, an immediate and considerable reduction in the $SO_3$ present, the composition of the precipitate being substantially that of a double oxide of nickel and calcium, a small amount only of calcium sulphate being present. Thus, in the two cases, we get $10NiO, 2CaO, 0.4CaSO_4$ and
$$10NiO, 3CaO, 0.6CaSO_4.$$
Whether the calcium sulphate would be entirely eliminated or not by a further increase in the amount of lime was not determined.

When the basic sulphate is precipitated in the presence of excess of sodium sulphate (Nos. 43 and 44), no sodium sulphate enters into its composition as it does in the analogous case with copper (Table III), but the proportion of calcium sulphate in it is increased instead, the partial saturation of the liquid by the sodium sulphate having, apparently, facilitated the abstraction of calcium sulphate from it. Clearly the tendency of basic nickel sulphate to combine with neutral sulphates is feeble as compared with that of basic copper sulphate.

It will be seen that in Nos. 43 and 44 the analytical numbers indicate that some of the $SO_3$ has been abstracted from the basic sulphate. The mixtures were left standing for several days after a portion of the liquid had been withdrawn for analysis, and it was found that the remaining liquid gradually assumed a green colour, the nickel passing slowly into solution again; doubtless some soluble double sulphate of nickel and sodium was being formed. The formation of a certain amount of such a compound before the liquid

had been withdrawn for analysis would account for the deficiency of $SO_3$ in the precipitate.

The examination of nickel sulphate having shown that it was not suitable for an investigation which was in contemplation, the subject was not pursued. The results, however, are sufficient to prove that, whilst the basic sulphates of different metals exhibit certain points of similarity in their behaviour towards excess of alkali and of neutral sulphates, each metal shows peculiarities of its own, and the actual products could only be determined by a separate examination in each case.

## Summary.

The substances formed on the addition of lime to copper sulphate, as in the preparation of Bordeaux mixture, are dependent on the proportions of lime used, and may be either (approximately so far as the $CaSO_4$ is concerned):

(1) $4CuO,SO_3,0\cdot06CaSO_4$,
(2) $5CuO,SO_3,0\cdot25CaSO_4$,
(3) $10CuO,SO_3,1\cdot3CaSO_4$,
(4) $10CuO,SO_3,4CaO,SO_3$,

(possibly 5) $10CuO,SO_3,10CaO,SO_3$, or (6) $CuO,3CaO$; that present in most cases probably being (4).

The fungicidal action of Bordeaux mixture seems to depend on the liberation of normal copper sulphate by the action of carbon dioxide on the basic sulphate. The action begins only after a certain lapse of time, the basic calcium sulphate having to be decomposed before the basic copper sulphate is attacked. By using only sufficient lime to form $4CuO,SO_3$, the presence of basic calcium sulphate, and the consequent delay in the action, is avoided; in addition to this, the amount of normal copper sulphate liberated (for a given amount of copper sulphate taken), and the insecticidal value of the mixture, will be two and a half times as great as when it consists of $10CuO,SO_3,4CaO,SO_3$.

To obtain the basic sulphate $4CuO,SO_3$, one gram of crystallised copper sulphate in solution must be precipitated by adding about 134 c.c. of lime-water. This mixture is rather more effective than the " normal " Bordeaux mixture, made with more than double the amount of copper sulphate precipitated by milk of lime in excess.

When copper sulphate is precipitated by lime in presence of excess of sodium sulphate, the precipitate contains sodium sulphate, as well as calcium sulphate; with the most basic sulphate, its formula is $10CuO,SO_4,2(Na_2,Ca)SO_4$, or $10CuO,SO_3,Na_2SO_4,CaSO_4$.

The basic sulphates of copper precipitated by soda contain no

appreciable amount of sodium sulphate, unless a large excess of sodium sulphate is present in the liquid. They therefore differ essentially from those obtained with lime, although the basicity is the same in the two cases.

Nickel sulphate with lime gives a basic sulphate containing a very little calcium sulphate, but if the lime is at all in excess, the basic sulphate is deprived of most of its acid, the precipitate consisting essentially of a double oxide of nickel and calcium. If excess of sodium sulphate is present in the liquid, the precipitate contains more calcium sulphate, but the results are complicated by some of the nickel redissolving to form (probably) a double sulphate of nickel and sodium.

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