CCXLV.—*A Study of the Basic Copper Sulphates.*

By GEORGE FOWLES.

THE literature of the basic copper sulphates contains many conflicting statements and describes many reputed compounds. Identical processes and seemingly identical conditions of working do not yield products of identical composition : thus, in five different papers five different compositions are found assigned to the basic salt obtained by boiling an unsaturated solution of copper sulphate, *viz.*, $CuSO_4,2Cu(OH)_2$ (Pickering, *Chem. News*, 1883, **47**, 181); $4CuSO_4,7Cu(OH)_2$ (Clowes, *ibid.*, 1898, **78**, 155); $3CuSO_4,5Cu(OH)_2$ (Schütze, *Pharm. Zentr.*, 1887, **8**, 295); $CuSO_4,3Cu(OH)_2$ (Hampe, *Z. Berg. Hütten. Sal.*, 1873, **21**, 268); a solid solution of varying composition (Young and Stearn, *J. Amer. Chem. Soc.*, 1916, **38**, 1947). Similar discrepancies occur in papers of modern date, in which the chemical individuality of these basic salts has been investigated by phase-rule methods. Young and Stearn (*loc. cit.*), from a study of the system $CuO–H_2O–SO_3$, conclude that the most basic salt that can exist at 25° is $CuSO_4,2Cu(OH)_2$ and that others recorded in the literature, such as $CuSO_4,3Cu(OH)_2$, are mixtures of this and free hydroxide. Bell and Taber (*J. Physical Chem.*, 1908, **12**, 171), who studied the same system under the same conditions, claim that no definite basic salt exists at 25°, but only a series of solid solutions, the most basic of which would have a composition $CuSO_4,2{\cdot}5Cu(OH)_2$. More recently, Britton stated

(J., 1925, **127**, 2796) that $CuSO_4,3Cu(OH)_2$ is the only complex that can exist at 25° and that the others are mixtures of this and free copper sulphate.

A study has now been made of the hydrolysis of solutions of copper sulphate and this has revealed the cause of most of the perplexing anomalies in the literature; thus it has been found that :

(*a*) The basic copper sulphates have the habit of forming highly stable intermediate products; consequently the chemical actions involved in their formation often reach equilibrium extremely slowly, so that the intermediate products or mixtures of these and the final products have been mistaken for definite compounds or classed as solid solutions.

(*b*) Basic salts have been discovered which are stable in copper sulphate solutions only above a certain concentration and are decomposed on dilution or on washing with water.

(*c*) When obtained by precipitation, these basic salts pass through a variety of forms (with a rapidity dependent on the conditions prevailing) so that a formula considered to represent a single phase may actually stand for a solid solution of several kinds of molecules of varying solubility and activity (compare Allmand, J., 1910, **97**, 608; Fowles, *Chem. News*, 1924, **128**, 2).

(*d*) When these basic salts are prepared by fractional precipitation with alkaline reagents, concurrent reactions take place, giving rise to at least two compounds which closely resemble each other in chemical and physical properties so that mixtures have been mistaken for single substances.

The Basic Salt obtained by Hydrolysis.—The composition of the salt obtained by boiling solutions of copper sulphate for a short time is compared, in the table, with that of previous workers.

Observer.	Duration of boiling.	Conc. used. $CuSO_4,5H_2O$ (g. in 100 c.c.).	$Cu : SO_4$ in product.	Formula assigned.
Hampe.	No details given.		Not given.	$CuSO_4,3Cu(OH)_2$.
Pickering.	15 mins.	Various 1·3 to 20	(Mean of five) 2·81 : 1	$CuSO_4,2Cu(OH)_2,\frac{1}{2}H_2O$.
Schütze.	No details given.		2·66 : 1	$3CuSO_4,5Cu(OH)_2,3H_2O$.
Clowes.	A few mins.	Not given.	2·75 : 1	$4CuSO_4,7Cu(OH)_2,H_2O$.
Kruger.	60 mins.	5 to 40	(Mean of four) 2·83 : 1	$CuSO_4,2Cu(OH)_2$.
Fowles.	15 mins.	5 10	2·78 : 1 2·80 : 1	$5CuSO_4,9Cu(OH)_2,2H_2O$.

The mean of many experiments of my own shows that the product contains copper and sulphate in the ratio $Cu : SO_4 = 2{\cdot}8 : 1$ [requiring a formula $5CuSO_4,9Cu(OH)_2$] and this finds support in the next series of experiments and in the analytical figures of Pickering and of Kruger (*J. pr. Chem.*, 1924, **108**, 278), although these authors round them off to fit the simple formula : with only copper and sulphate to be estimated in the products, the analytical accuracy justifies the retention of the fractional value.

The still lower ratios obtained by Clowes and by Schütze are possibly due to small amounts of iron in the copper sulphate used, the presence of which would enhance the sulphate content and depress that of the copper. Clowes used commercial copper sulphate which he purified by recrystallising it several times from water, a procedure which fails to remove the iron. Now the amount of basic salt obtained by hydrolysis is very small (Pickering estimates it as varying from 0·4 to 2·0% of the copper salt taken), but owing to its higher insolubility the whole of the iron is precipitated, and although it constitutes only a trifling percentage of the original salt, its amount becomes appreciable when concentrated in the hydrolysis precipitate.

The Production of the Hydrolysis Salt in Quantity.—This is effected by suitably removing the acid set free by hydrolysis, and of the substances tried for this purpose sodium nitrite has proved to be by far the most satisfactory. Other salts such as sodium formate, carbonate, etc., are not so suitable, for the precipitate is always contaminated with small amounts of basic copper formate, etc., which is only removed by prolonged boiling with copper sulphate, a procedure which alters the composition of the product : bases cannot be used at all, as they form stable intermediate compounds. The action of sodium nitrite is unique : an immediate precipitate does not form, but a deep green liquid complex is produced from which, on boiling, the basic salt is rapidly and abundantly precipitated in fine microscopic crystals which quickly settle and are easily washed.

The following ratios of Cu : SO_4 were found in the products obtained from various concentrations of copper sulphate, represented as g. per 100 c.c. of water. In every case the copper sulphate was in excess so that the liquid was always acidic : the precipitates were free from nitrite.

$CuSO_4,5H_2O$	125	90	75	75	30	5
Cu : SO_4	2·77	2·79	2·81	2·79	2·81	2·81

Similar figures were obtained when quinoline was used in the place of sodium nitrite, but the products were slimy and difficult to wash. This constancy of composition over a wide range of concentration seems to preclude the possibility that the product is $CuSO_4,2Cu(OH)_2$ with adsorbed copper sulphate, and indicates that

$5CuSO_4,9Cu(OH)_2$ is a definite compound. A series of extractions with *N*/10-sulphuric acid showed an unchanged copper content, whilst in a control experiment with a mixture of the alleged $CuSO_4,2Cu(OH)_2$ and $CuSO_4,3Cu(OH)_2$ the amount of copper extracted gradually increased.

The Product obtained by Prolonged Boiling.—When the boiling is prolonged, the simple 1 : 2 compound is obtained. Various concentrated (but not saturated) solutions were refluxed for 48 hours and the basic salt precipitated contained $Cu : SO_4 = 2{\cdot}94 : 1$. Ipatiev and Werklowsky (*Ber.*, 1911, **44**, 1755) found $Cu : SO_4 = 2{\cdot}94 : 1$ in the basic salt obtained by digesting *N*/10-copper sulphate for a week at 100°. Smith (*Mems. Chem. Soc.*, 1843, **5**, 221) heated copper hydroxide with excess of copper sulphate in one experiment for 48 hours and in another for 10 weeks and found $Cu : SO_4 = 2{\cdot}97 : 1$ in the resulting basic salt. Young and Stearn (*loc. cit.*) heated copper oxide in solutions of copper sulphate at 25°, 37·5°, and 50° until equilibrium was attained (15 to 88 days). The products obtained (as shown in the recalculation of their results, p. 1857) contained $Cu : SO_4$ exactly 3·0 : 1. From these results it follows that the final product of the hydrolysis of unsaturated solutions of copper sulphate is the 1 : 2 salt: in the prolonged experiments in which copper oxide was added, any intermediate compounds which might have been formed would have been decomposed, so the copper oxide would merely neutralise the acid set free and augment the hydrolysis. The 5 : 9 salt which is precipitated on boiling for a short time is therefore an intermediate compound, and a specimen refluxed for 24 hours with a strong solution of the normal salt was converted into the 1 : 2 compound.

Isolation of a New Basic Copper Sulphate.

In studying the effect of concentration on the composition of the basic salt formed by hydrolysis an extreme case was investigated—that of a saturated solution at its boiling point (104°) in the presence of solid copper sulphate. The product obtained is interesting in that it is decomposed by water. It is precipitated in green, rhombic tablets, crystalline to the naked eye: it has not been described before [Found: Cu, 39·3; SO_4, 38·6; H_2O, 18·5. $2CuSO_4,Cu(OH)_2,4H_2O$ requires Cu, 39·3; SO_4, 39·0; H_2O, 18·5%]. It can be prepared in solutions not fully saturated and is therefore stable over a small range of temperature and concentration. Cold water slowly decomposes this salt, giving an insoluble basic salt and a solution of copper sulphate: more copper sulphate is extracted by cold water than by hot—convincing testimony that this salt in not an insoluble product with adhering copper sulphate. Besides its colour and crystalline form and its behaviour with water, further chemical evidence exists to support its claim to individuality. Analyses of different preparations yield concordant figures and the ratio Cu : SO_4 is a simple one. The salt is scarcely acted upon in the cold by a mixture of glycerol and methyl alcohol, a liquid which dissolves a considerable amount of copper sulphate. With excess of cold water (up to about 40°) its decomposition is expressed by the equation

$$3[2CuSO_4,Cu(OH)_2] = CuSO_4,3Cu(OH)_2 + 5CuSO_4.$$

With rise of temperature the insoluble salt obtained becomes less basic : at 95° it has the composition $CuSO_4,2{\cdot}5Cu(OH)_2$. Ignorance of the existence and behaviour of this 2 : 1 salt has probably lead to errors; thus Young and Stearn (*loc. cit.*, p. 1952), who employed conditions which should have yielded this salt, washed their product with water, thereby failing to isolate it.

The Action between Copper Hydroxide and a Solution of Copper Sulphate.

Formation of a basic salt readily takes place when copper hydroxide is added to a solution of copper sulphate, for, when the hydroxide used is freshly prepared and still moist, it goes pale green when it enters the liquid, and on filtering forthwith no copper can be found in solution if a slight excess of the hydroxide has been used. The product from an excess of unsaturated solution had the average composition Cu : SO_4 = 3·8 : 1. In the cold the action is slower, requiring a few days in a 1% solution, but only a few minutes in a highly concentrated solution. The composition of the product varied from 3·92 : 1 for the most dilute solution used (initial concentration 0·8, final 0·4%) to 3·68 : 1 for a 20% solution. The basic salt obtained by this method has always passed in the literature as the 1 : 3 salt but it has been completely overlooked that the procedure would be expected to produce the 1 : 2 salt in abundance by continuous removal of the acid set free in the reaction

$$3CuSO_4 + 4H_2O = CuSO_4,2Cu(OH)_2 + 2H_2SO_4.$$

Again, from considerations of the phase rule the co-existence of both the 1 : 2 and the 1 : 3 salts in a boiling unsaturated solution of the normal salt is incompatible, since the system cannot be in equilibrium with two solids phases. The product is therefore metastable and, from a consideration of the limits of its varying composition, it is seen to be a mixture of the 1 : 2 salt formed by hydrolysis and the 1 : 3 salt formed by direct union of the hydroxide and sulphate in solution.

When precipitated from a boiling solution the 1 : 3 salt is microcrystalline, and the stability of this form is remarkable. It can be boiled in dilute solutions of copper sulphate for hours without undergoing any change in composition, and agitation in solutions of copper sulphate at 25° to 50° for several months has little effect upon it as shown by the experiments of Bell and Taber (*loc. cit.*), Britton (*loc. cit.*), and the author; but when refluxed for 24 hours in a strong solution (75 g. of crystals in 100 c.c. of water), it was converted completely into the 1 : 2 salt. This important experiment was repeated successfully several times with specimens of the 1 : 3 salt prepared by different methods. Although, from other experiments, it is believed that the 1 : 2 salt is the phase stable in cold solutions, all attempts to detect any change in composition when the 1 : 3 salt has been left in contact with cold solutions have failed. Copper hydroxide was placed in a large volume of dilute copper sulphate solution and after a few days a fraction of the liquid was withdrawn and the copper estimated, and although this was continued until the liquid was exhausted (3 months) the readings remained uniform. One specimen was unchanged in composition after standing for a year in a concentrated solution. Specimens of the 1 : 3 salt which had stood in saturated solutions for 4 years, and even (owing to the incidence of the war) for 10 years, could not be washed; originally microcrystalline and rapidly settling, they had become slimy and colloidal and were of the consistency of paint. The high stability of the 1 : 3 salt is perhaps due to the changes it undergoes after precipitation. It can be obtained in a blue gelatinous form which on standing passes into the pale green, crystalline variety; these changes are no doubt accompanied by a decrease in solubility and chemical reactivity, so that where it has been assumed that the formula $CuSO_4,3Cu(OH)_2$ stood for a single phase it may actually have represented a solid solution of two or three different kinds of molecules.

This primary precipitation of an intermediate phase and its slow change into the final phase seems to be characteristic of copper compounds. It is well known that the more basic carbonate, $2CuCO_3,3Cu(OH)_2$, obtained by precipitation with sodium carbonate, on standing in the preparation liquor changes into the less basic malachite, $CuCO_3,Cu(OH)_2$: the more basic copper formate, the 1 : 3 salt, on standing in a cold solution of the normal salt passes in a few weeks into the less basic 1 : 2 salt (J., 1915, **107**, 1281). An analogous behaviour is exhibited by copper hydroxide; the blue, unstable, gelatinous variety passes first into the stable crystalline form, then slowly during several years into dark coloured varieties before turning into the black indefinitely hydrated oxide CuO,xH_2O

and finally into CuO (*Chem. News*, 1924, **128**, 2). Allmand (*loc. cit.*) has shown that, whereas the solubility of crystalline cupric hydroxide is 3 × 10^{-7} g.-mol. per litre, cupric oxide is still more insoluble and decreases in solubility according to its age and temperature of preparation.

When, therefore, copper hydroxide is added to a solution of copper sulphate there is a concurrence of several reactions: the neutralisation of the acid of hydrolysis with precipitation of the 1 : 2 salt, the formation of the 1 : 3 salt by direct union, the change of the 1 : 2 and 1 : 3 salts into less soluble and less reactive forms, and the conversion of the 1 : 3 into the 1 : 2 salt by the action of copper sulphate. It would thus seem impossible, working in a solution of copper sulphate, to prepare the 1 : 3 salt quite free from the 1 : 2 compound; but in liquids where the concentration of the copper sulphate is ether nil or very low, pure 1 : 3 salt can be obtained. These conditions particularly prevail when copper hydroxide is placed in a saturated solution of ammonium sulphate. In such a liquid the solubility of the copper sulphate is enormously depressed and the small amount of copper in solution may all belong to the complex compound. From this liquid the basic salt separates out in a few days and contains Cu : SO_4 exactly 4 : 1. When dried in the air, the product is pale greenish-blue of formula $CuSO_4,3Cu(OH)_2,xH_2O$, where x is less than 1, but when this is heated at 160° for a few hours (this can be safely done, for the water of the hydroxyl groups is not removed below about 300°) water is given off, and the colour changes to green, the tint of chromium oxide. The green compound has the composition $CuSO_4,3Cu(OH)_2$, identical with that of the purest specimens of the mineral brochantite.

The Action between Copper Oxide and a Solution of Copper Sulphate.

Contrary to expectation, copper oxide does not yield the same product as copper hydroxide. Ignited copper oxide was placed in a strong solution of copper sulphate at the ordinary temperature. It very slowly changed in colour, but at the end of 3 years it was visibly homogeneous, considerably more voluminous, and of the pale green tint of the basic salts. At the end of 4 years, when it was removed and analysed, it had exactly the composition of the 1 : 2 salt. The recalculated results of Young and Stearn show that when copper oxide is heated in strong solutions of copper sulphate at 25° to 50° for long periods the 1 : 2 salt is always obtained. The series of experiments of these authors at 50° was repeated but, as a control, copper hydroxide (the blue crystalline variety) was placed in a similar solution in the same thermostat. Where copper oxide was used, the basic salt contained Cu : SO_4 = 2·97 : 1, but with copper hydroxide the ratio was 3·83 : 1. Copper oxide (obtained by the gentle ignition of the hydroxide) in a cold solution of copper sulphate formed a product with Cu : SO_4 = 3·75 : 1. Sebatier claimed to have formed the 1 : 3 salt by digesting the brown hydrated oxide with copper sulphate, but he arrived at his formula by an estimation of the copper only (*Compt. rend.*, 1897, **125**, 101). Kruger (*loc. cit.*), realising that the analytical procedure was unsatisfactory, repeated the experiments employing Sebatier's conditions, and his analyses show Cu : SO_4 = 3·66 : 1. It is here suggested that the different behaviour of the oxide and hydroxide is due to the difference in solubility already mentioned. The hydroxide apparently dissolves and unites with copper sulphate to form the 1 : 3 salt, but sufficient copper oxide does not dissolve to exceed the solubility of the 1 : 3 salt. The slow formation of the 1 : 2 compound points to the conclusion that a slow solution of the copper oxide in the acid of hydrolysis precipitates the 1 : 2 salt in equilibrium with this acid. The brown hydrated oxide and the oxide obtained by gentle ignition act as if they were solid solutions of molecules, some having the reactivity of the hydroxide and some that of the oxide. It is now possible to offer an explanation of the discordant results of Young and Stearn and Bell and Taber, who studied the same system under the same conditions. The former workers used only copper oxide in their experiments and thus always obtained the 1 : 2 salt: the latter investigators reasonably considered it to be a matter of indifference, in the system $CuO–SO_3–H_2O$, whether copper oxide was added as such or in the form of the hydroxide, and so they used either indiscriminately; consequently in some experiments they formed the 1 : 2 salt and in others the 1 : 3 salt, which by long digestion was partly converted into the 1 : 2 compound; hence the solid phases appeared to them to be a series of solid solutions, of which the most basic would require a formula $CuSO_4,2{\cdot}5Cu(OH)_2$.

The Action between Copper Sulphate and Soluble Bases.—The method of adding a soluble base to a solution of copper sulphate in quantity insufficient to precipitate all the copper as hydroxide is the one most generally employed to prepare basic salts. This, however, is most unsatisfactory, for, not only are all the concurrent reactions possible which were revealed by the study of the action between copper hydroxide and sulphate, but, in addition, there is the danger of forming compounds of the foreign metal, such as $3CuSO_4,K_2SO_4,Cu(OH)_2$ (Brunner, *Pogg. Ann.*, 1829, **15**, 476) and the various basic compounds containing both copper and calcium found by Pickering in his investigation of Bordeaux mixture (J., 1907, **91**, 1988). Moreover, Jordis found (*Z. Elektrochem.*, 1912, **18**, 553) that when caustic soda is used in the cold as precipitating reagent the product always contains sodium, often in considerable amount, which cannot be removed by washing. No attempt is made to criticise in detail the many papers dealing with this section of the work or to harmonise the discordant results : where the conditions used are given, it can usually be seen that a product of the composition claimed was the one likely to be formed. It is generally stated that the addition of less than 0·75 equiv. of soluble base results in the formation of the 1 : 3 salt, and under certain conditions the product obtained undoubtedly consists almost wholly of this salt, but from the considerations outlined above it is doubtful whether the 1 : 3 salt completely free from the 1 : 2 salt can be obtained by this method. Williamson (*J. Physical Chem.*, 1923, **27**, 789) has recently studied this action, but he only prepared one basic salt by two single precipitations with caustic soda. On this meagre experimental foundation he bases a lengthy criticism of papers on the basic copper sulphates. He seems unaware of the elaborate work of Pickering and of Jordis, or that his experiments confirm those of Proust (*Ann. Chim.*, 1800, **32**, 34). His basic salt contained Cu : SO_4 = 3·8 : 1 instead of the expected 4 : 1 and this he attributes to his own inadequate washing or to adsorption of copper sulphate. Although no experiment is adduced here which definitely refutes the adsorption explanation, it is not convincing, being purely conjectural, and its adoption excludes the more plausible explanations which have experimental evidence to support their claim to consideration.

The 1 : 3 salt seems to be formed whenever hydroxide is added to copper sulphate solution and its formation is favoured by low concentration and low temperature when the inimical reactions are hindered or suppressed. It is best prepared in basic solutions where the copper and sulphate radicals form part of complex ions and where there is little or no actual concentration of copper sulphate. Thus Kruger obtained the 1 : 3 compound by using a large excess of sodium acetate, formate, etc., but in my own experiments with these reagents the 1 : 3 salt was always contaminated with small amounts of basic copper acetate, etc. Casselmann noticed the same thing (*Z. anal. Chem.*, 1865, **4**, 29). The 1 : 2 salt is produced from a solution in which copper sulphate is in excess, therefore it requires a solution which is acidic; its formation is favoured by high concentration and high temperature. It is maintained that the 1 : 2 salt is the solid phase in equilibrium with the acid of hydrolysis in a solution of copper sulphate, for this is the basic salt produced whenever the acid is removed otherwise than by the direct addition of hydroxide. Thus when excess of copper sulphate solution containing sodium nitrite is allowed to stand in the cold, a small crystalline precipitate appears after some days and very slowly increases in quantity. From such a medium (containing 20% of hydrated copper sulphate) the basic salt was not removed until 8 years had passed, when it was analysed and found to be the 1 : 2 salt.

Production of the Unstable Salt, $2CuSO_4,3Cu(OH)_2$.—When an attempt was made to expedite the reaction by removing the nitrous acid by the use of urea, the result was unexpected, for it disclosed an easy method of preparing the 2 : 3 salt described by Sebatier (*loc. cit.*). When to an excess of a cold saturated solution of copper sulphate some sodium nitrite is added followed by urea, a precipitate falls in abundance in a few days at the ordinary temperature or in a few hours at 30°. It can be washed rapidly with cold water or more slowly and safely with a mixture of glycerol and methyl alcohol. Analysis shows that it requires the above formula. Sebatier states that it is decomposed by cold water according to the equation

$$2CuSO_4,3Cu(OH)_2 = CuSO_4,3Cu(OH)_2 + CuSO_4,$$

but he did not further investigate its behaviour. In the cold it decomposes as Sebatier states, but with hot water the insoluble residue consists largely of the 1 : 2 salt: thus at 85° it had the composition $CuSO_4,2{\cdot}2Cu(OH)_2$. On the following grounds this salt is considered to be a distinct compound:

(1) Analysis of various preparations show $Cu : SO_4 = 2{\cdot}5 : 1$.

(2) It cannot be a mixture of copper sulphate and the 1 : 3 salt, for the amount of copper sulphate extracted by water decreases with rise of temperature and conversely.

(3) The salt is almost insoluble in a mixture of equal volumes of glycerol and methyl alcohol, and therefore contains little, if any, free copper sulphate.

The Naturally Occurring Compounds.—The best known of these is brochantite, to which several conflicting formulæ have been assigned: in Dana's "System of Mineralogy" (1889) twelve analyses are given, no two of which are concordant. This is probably due to the rarity of pure specimens of the mineral and to the mineralogists being unaware of the existence of another distinct, naturally occurring compound, antlerite. However, Ford (*Amer. J. Sci.*, 1910, **30**, 24) obtained from the region of Collahurase, Chili, some crystals of brochantite which he described as being of ideal purity: they were large enough for him to take the usual crystallographical measurements and to perform analyses in duplicate. His concordant figures agree well for those demanded by $CuSO_4,3Cu(OH)_2$.

This formula for brochantite is supported by the analyses by Arzruni and Thaddéeff (*Z. Kryst. Min.*, 1899, **31**, 229) of a good specimen which, corrected for less than 3% of foreign matter, gave Cu : SO_4 : H_2O = 4 : 1 : 2·95, and by Hillebrand (*Bull. U.S. Geol. Survey*, No. **591**, p. 359) of one containing less than 2% of foreign matter which gave similar figures. Synthetical brochantite therefore is not the 1 : 3 salt as usually precipitated, in which case it contains Cu : SO_4 : H_2O = 4 : 1 : 4, but the product obtained by heating this precipitate for some hours at 160—180°, when it loses water and changes from bluish-green to a decided green colour like that of chromium oxide. In 1889 Arzruni and Thaddéeff (*loc. cit.*) examined a new, naturally occurring basic copper sulphate which they named "stelznerite." Its state allowed of a satisfactory crystallographical characterisation, and a sufficient quantity of high purity (99%) was available for several analyses, which showed Cu : SO_4 = 3·01 : 1. Now Hillebrand had obtained Cu : SO_4 = 3·3 : 1 and 3·1 : 1 from the analyses of a variety of brochantite from Arizona which he had named "antlerite." At the suggestion of Clarke the two minerals were optically examined by Schaller (*Amer. J. Sci.*, 1910, **29**, 311), who found that they were identical but different from brochantite.

The basic salts which from the author's results seem to be definite compounds are tabulated below: hydrates of these and varieties in which copper hydroxide is replaced by the oxide are not included.

Formula.	Appearance.	In water.	In copper sulphate solution.
(i) $CuSO_4,2Cu(OH)_2$ (Antlerite).	Pale bluish-green, microcrystalline.	Insoluble and stable.	Stable in hot strong solutions.
(ii) $CuSO_4,3Cu(OH)_2$ (Brochantite).	Pale green (bluish-green when hydrated), microcrystalline.	,, ,,	In hot strong solutions passes into (i).
(iii) $5CuSO_4,9Cu(OH)_2,2H_2O$.	Pale bluish-green, microcrystalline.	,, ,,	,, ,,
(iv) $2CuSO_4,Cu(OH)_2,4H_2O$.	Pale emerald green, crystalline.	Decomposed, yielding salts (i), (ii), and $CuSO_4$.	Can exist only in solutions saturated or nearly so at the boiling temperature.
(v) $2CuSO_4,3Cu(OH)_2$.	Pale blue.	,, ,,	Stable only in cold strong solutions.

EXPERIMENTAL.

Most of the experiments mentioned are so simple that no detailed description is needed. Copper and sulphate were estimated by well-accredited methods, and volumetric methods were generally but not exclusively employed. Throughout this paper the analyses are expressed as the ratio Cu : SO_4 (and where the results of other workers are quoted they have been converted into this form).

Unfortunately, in some papers only copper was estimated and a formula was constructed or selected to fit the result; such a procedure is unsound, for the water content varies with the method of preparation—a phenomenon probably connected with the variable nature of the solid phases concerned. Water was not estimated directly: it was found that the water of constitution is lost only slowly at 300—400°, at which temperature further decomposition of the salt has already begun. The copper hydroxide used was the blue crystalline variety prepared after the method of Böttger. A method was devised of estimating the ratio Cu : OH directly in those salts not decomposed by water: a small excess of the basic salt was placed in a definite volume of standard sulphuric acid and when, after a few days, equilibrium was established, the copper in solution was estimated.* The results were repeatedly checked by other methods and found to be quite accurate, moreover the method is time-saving and especially valuable when only a small amount of salt is available.

Discussion.

Young and Stearn (*loc. cit.*), who studied the system CuO–SO_3–H_2O at 25—50°, found that no definite basic salts existed but only a series of solid solutions. They added ignited copper oxide to solutions of copper sulphate and heated them at the given temperatures until equilibrium was attained (88 days). The solid phases were separated by centrifuging and analysed without further treatment. The results revealed a series of solid solutions. This conclusion has been several times quoted in support of other arguments, but, as will be shown below, it is highly probable that the authors misinterpreted their experimental work by the employment of an unsound analytical procedure. Sufficient data are available in their paper for calculating the composition of the solid phases by an indirect method; thus, they give the initial and final concentrations of the copper sulphate, and the weight of the copper oxide added, hence the copper sulphate which has left the liquid is attached to the copper oxide. The recalculation (two series only are shown here, but all yield similar results) shows the high degree of accuracy of the experimental work, and the mean of the concordant results yields a ratio Cu : SO_4 of exactly 3 : 1, showing that the solid phase was always the 1 : 2 salt and not the series of solid solutions announced. The result indicated by the recalculation was confirmed by a repetition of the experiments at 50°, but using the indirect method of analysis.

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* Britton (*loc. cit.*, p. 2800) employed a similar method to show the homogeneity of his 1 : 3 salt.

Recalculation of Young and Stearn's Results.

Mols. of $CuSO_4$ taken.	Mols. of CuO taken.	Mols. of $CuSO_4$ in solution at end.	Mols. of $CuSO_4$ in solid phase.	$\frac{Cu(OH)_2}{CuSO_4}$ in solid phase.	Composition assigned by Y. and S.
		(i) At 25°.			
0·10368	0·02592	0·09042	0·01326	$\frac{2592}{1326} = 1{\cdot}96$	1·35 : 1
0·10368	0·05184	0·07579	0·02789	$\frac{5184}{2789} = 1{\cdot}86$	1·38 : 1
0·10368	0·10368	0·05186	0·05182	$\frac{10368}{5182} = 2{\cdot}00$	1·55 : 1
0·10368	0·20736	0·00132	0·10236	$\frac{20736}{10236} = 2{\cdot}03$	1·84 : 1
		(ii) At 50°.			
0·10368	0·02592	0·09141	0·01227	$\frac{2592}{1227} = 2{\cdot}11$	1·28 : 1
0·10368	0·05184	0·078197	0·02548	$\frac{5184}{2548} = 2{\cdot}03$	1·31 : 1
0·10368	0·10368	0·05163	0·05205	$\frac{10368}{5205} = 1{\cdot}99$	1·31 : 1
0·10368	0·20736	0·00085	0·10283	$\frac{20736}{10283} = 2{\cdot}02$	1·83 : 1

Britton (*loc. cit.*) has recently studied the same system CuO–SO_3–H_2O at the same temperature, 25°, but has reached an opposite conclusion. Young and Stearn state that no salt as basic as $CuSO_4,3Cu(OH)_2$ can exist, whereas Britton states that the only basic salt at 25° is this salt. Britton started with the 1 : 3 salt and copper oxide as his solid phases, but in half his experiments the final liquid phase was water, and in half the remainder it was a very weak solution of copper sulphate, *i.e.*, he employed conditions in which it was impossible for the highly stable intermediate compound 1 : 3 to pass into the final stable 1 : 2 salt. It is significant that on a large-scale graph the tie-lines from the two most concentrated liquid phases meet at a point where $Cu : SO_4 = 7 : 2$ (corresponding to 1 : 2·5) before passing near the point representing the 1 : 3 salt, suggesting that where the conditions were most favourable some conversion into the 1 : 2 salt had taken place. The composition of the " rest " from the most concentrated solution is miscalculated (it should be 0·423, not 0·314 as given), therefore the comment based on the erroneous figure is irrelevant (p. 2802). Consequently the contention that the 1 : 3 salt is the only basic salt of copper cannot be considered as established by Britton's experiments. His later statement (unsupported by further experimental evidence) that the 1 : 2 salt is " undoubtedly a mixture of the 1 : 3 salt and copper sulphate " is sufficiently refuted by the well-established individuality of its naturally occurring form, antlerite, by its preparation, and by other evidence given in this paper.

Addendum.—Bell and Murphy have just published a paper entitled " Basic Copper Sulphate at 100° " (*J. Amer. Chem. Soc.*, 1926, **48**, 1500) in which they assert that the 1 : 3 salt is the only basic salt stable in the presence of copper sulphate at 100°. Here once again the metastable 1 : 3 salt has been mistaken for the final equilibrium product. The authors heated copper oxide in solutions of copper sulphate and state that equilibrium was reached in 6 hours. It is obvious from a scrutiny of their figures that the solid residue consisted mostly of the 1 : 3 salt whilst the liquid was a weak solution of copper sulphate, in which the 1 : 3 salt would pass extremely slowly into the 1 : 2 salt. It has been established conclusively in the body of the present paper that the boiling of an unsaturated solution of copper sulphate produces the 1 : 2 salt, and there can be only one solid phase in this system. In the second series of experiments Bell and Murphy heated copper oxide for 8 hours at 100° in solutions of copper sulphate of various concentrations. The determination of the composition of the solid phases by Schreinemakers's method was abandoned because the tie-lines formed such a narrow pencil that it was impossible to locate with certainty the point of convergence (compare the criticism of Britton, p. 1857), and the solid phases were analysed after being washed with water. This procedure is unsound, since the 2 : 1 salt which forms in some concentrations is decomposed by water. The only analysis quoted reveals a ratio $Cu : SO_4 = 3{\cdot}8 : 1$. It is therefore apparent that their product consisted mostly of the 1 : 3 salt, formed by direct union (so presumably the oxide had not been strongly ignited), mixed with some 1 : 2 salt formed by the hydrolysis of the copper sulphate. Consequently equilibrium was never attained and the statement that the 1 : 3 compound is the basic salt stable at 100° is not correct.

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