CCCLXXXII.—*The Basic Sulphate of Copper. A Reply.*

By Hubert Thomas Stanley Britton.

Fowles (this vol., p. 1845) claims to have found " the cause of most of the perplexing anomalies " relating to the numerous basic sulphates of copper which have been reported, but in so doing he has added two more to their number, although he has not advanced any satisfactory proofs of their individualities. It is not justifiable to call any basic substance a " compound " until its fixity of composition and conditions of existence have been ascertained. Constancy of composition may be only apparent owing to the reproduction of some essential condition during the formation of the precipitate, *e.g.*, the hydrogen-ion concentration. Fowles's paper contains many unsubstantiated statements, especially in regard to the importance and application of the phase rule to the study of basic salts. He claims to have isolated a new basic sulphate, $2CuSO_4,Cu(OH)_2,4H_2O$, by boiling a saturated copper sulphate solution " in presence of solid copper sulphate," or " from solutions not fully saturated," and he states that the salt is " therefore stable over a small range of temperature and concentration." It is difficult to understand how the composition of a precipitate, formed in such concentrated solutions, could be determined, seeing that it is decomposed on treatment with water. Again, the product, $5CuSO_4,9Cu(OH)_2$, is stated to be formed by boiling for a short time solutions either of copper sulphate or of copper sulphate to which sodium nitrite has been added, whereas if the boiling be prolonged $CuSO_4,2Cu(OH)_2$ is obtained, a substance which Fowles maintains to be "the solid phase which is in equilibrium with the acid of hydrolysis in a solution of copper sulphate."

During recent years four attempts have been made to ascertain which of the many recorded basic sulphates are actual compounds by a study of the relevant section of the ternary system $CuO–SO_3–H_2O$. Three of these attempts were made at 25° by Bell and Taber (*J. Physical Chem.*, 1908, **12**, 171), Young and Stearn (*J. Amer. Chem. Soc.*, 1916, **38**, 1947; also at 37·5° and 50°), and the author (J., 1925, **127**, 2796). In the first two studies, somewhat inert substances were used which could only attain equilibrium slowly and with difficulty, and it is doubtful whether true equilibrium was ever attained. In Bell and Taber's work, however, one Schreinemakers tie-line passes quite close to the point corresponding to $4CuO,SO_3,4H_2O$. Young and Stearn made complete analyses, which were not always concordant, of the unwashed solid phases and of the copper content of the liquid phases. Fowles, disputing their results for the solid phases, has recalculated their compositions from the change in concentration of the liquid phases, and considers the results to afford valid evidence of the existence of $CuSO_4,2Cu(OH)_2$, in spite of the fact that the actual analytical data give values ranging from 1·28 to 1·84 mols. of $Cu(OH)_2$ to each mol. of $CuSO_4$. Fowles refers to Young and Stearn's analyses of their so-called solid phases as being vitiated probably owing to the "employment of an unsound analytical procedure," but he regards the analyses of the liquid phases as showing "the high degree of accuracy of the experimental work." It is obvious that much of the difference was due to the fact that Young and Stearn regarded the "rests" as the solid phases, but throughout Fowles's paper it appears that he has done the same thing, especially where concentrated solutions and unstable salts were involved. As stated in the author's paper, the precipitate, $4CuO,SO_3,4H_2O$, formed when alkali (not exceeding 0·75 equiv.) is added to a dilute solution of copper sulphate with continuous shaking, can easily be washed free from impurities, and there is no "danger of forming compounds of the foreign metal" (Fowles, pp. 1852—3). The author has always obtained this salt in a non-gelatinous state, and never in the gelatinous state mentioned by Fowles. If, however, the alkali is added without the necessary precautions being taken, a gelatinous precipitate of copper hydroxide retaining appreciable amounts of sulphate will be obtained, and may sometimes fortuitously contain CuO and SO_3 in the ratio 4 : 1. In the author's experiments, equilibrium was rapidly established through the use of more reactive substances than had been employed hitherto, *viz.*, sulphuric acid, moist basic sulphate, and moist hydrated copper oxide, and the quantities used were so adjusted that the amounts of solid phases were as small as possible in order to ensure that they should enter completely into equilibrium. In the opinion of the author, there is no doubt that the analyses given actually represent states of true equilibrium. It should scarcely be necessary to remark that the compositions of the liquid and solid phases at the final equilibrium are quite independent of the substances used, whether they be copper oxide, which has been ignited or not, or copper hydroxide; the choice of substances affects only the time required for equilibrium. Fowles, however, attempts to harmonise the conflicting results of Young and Stearn and of Bell and Taber by making such unjustifiable assumptions and, moreover, states that the substances used by the author were such as to make it "impossible for the highly stable intermediate compound $CuSO_4,3Cu(OH)_2$ to pass into the final stable $CuSO_4,2Cu(OH)_2$ salt." He seems to have overlooked the fact that the present author also used partly dehydrated copper hydroxide in some experiments instead of the basic sulphate (*loc. cit.*, p. 2800), and again in every case the solid phase in equilibrium with copper sulphate solution as the liquid phase was $CuSO_4,3Cu(OH)_2,H_2O$. Had Fowles's contentions concerning reactions between copper hydroxide and copper sulphate solutions been correct, the use of hydrated copper oxide should have had some effect on the kind of basic salt obtained. Fowles states (p. 1851) that when "copper hydroxide is added to a solution of copper sulphate there is a concurrence of reactions : the neutralisation of the acid of hydrolysis with the 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 salt into the 1 : 2 salt by the action of copper sulphate." The whole of this statement is advanced without any supporting evidence. Fowles gives no data to show that solubility variations take place, and moreover (p. 1850) he even disproves the statement that the 1 : 3 salt passes into the 1 : 2 salt by the action of copper sulphate under ordinary conditions, for he admits that "all attempts to detect any change in composition when the 1 : 3 salt has been left in contact with cold solutions have failed." If it were likely that the neutralisation of the acid of hydrolysis would give rise to a basic salt different from that produced by the interaction with copper sulphate, the degree of hydrolysis of copper sulphate solutions is so very small that the proportion of basic salt due to that reaction would be too small for detection by the ordinary methods of chemical analysis.

Instead of accepting the evidence as to the composition of the basic sulphate given by the pencil of tie-lines as a whole in the author's phase-rule diagram, Fowles has taken exception to that afforded by the two corresponding to the two most concentrated liquid phases because, when drawn on a large scale, they do not intersect at the point $4CuO,SO_3,4H_2O$. One line passes almost through this point and the other lies at a distance of about a 1% division from it; when it is remembered that such a divergence is caused by an error of much less than 1% in the analysis of the "rest," it will be obvious that the source of the error most probably lies in the experimental method, one cause being the slight evaporation which takes place during the preparation of the "rest" for analysis. Had $CuSO_4,2Cu(OH)_2$ been a basic salt stable, as Fowles seems to think, in some concentrations of copper sulphate solution, then this would have been indicated by a pencil of tie-lines.

Many of the so-called basic salts containing a larger proportion of SO_3 appear to have been obtained from concentrated solutions, *e.g.*, $5CuO,2SO_3,xH_2O$ (Sabatier, *Compt. rend.*, 1897, **125**, 101; Fowles, *loc. cit.*, p. 1854), and this was shown by the author (*loc. cit.*, p. 2802) to be accounted for by mother-liquor adhering to the solid phase. The "rests" corresponding to the liquid phases containing 3·17 and 7·17% CuO were freed as far as possible from adhering liquor by suction, and yet the former contained 0·314 mol. of SO_3 and the latter, 0·423 mol. of SO_3 to each mol. of CuO.* The composition of the former "rest" happens to agree roughly with $3CuO,SO_3$, and the latter with $5CuO,2SO_3$, which both Sabatier and Fowles have considered to be a definite individual. There is no reason to believe that $CuSO_4,2Cu(OH)_2$ is a compound stable at 25° as stated by Fowles, even although a substance having approximately that composition may occur in nature, *viz.*, antlerite.

The fourth paper dealing with the phase-rule study of basic copper sulphate is that by Bell and Murphy (*J. Amer. Chem. Soc.*, 1926, **48**, 1500), who have worked out the 100°-isotherm and have

---

* The author's thanks are due to Mr. Fowles for directing attention to the fact that the latter "rest" contained 0·423 mol. of SO_3, and not 0·314 mol., which was misplaced in Table I. This, however, does not detract from the argument, as Fowles suggests, but, on the contrary, strengthens it.

found that the only basic sulphate which exists in stable equilibrium at that temperature is the one which the author found at 25°. Fowles states that Bell and Murphy have mistaken the "metastable" * $CuSO_4,3Cu(OH)_2,H_2O$ for the "final equilibrium product," and asserts that "equilibrium was never attained and the statement that the 1 : 3 compound [$CuSO_4,3Cu(OH)_2$] is the basic salt stable at 100° is not correct." As pointed out by Fowles, the method adopted by Bell and Murphy in arriving at the composition of the solid phases is open to objection, for had a basic salt been formed which is decomposed by water, washing before analysis would have given rise to erroneous results, although it is scarcely probable that washing would have been so protracted as to cause the complete transformation into $CuSO_4,3Cu(OH)_2$ in every case shown by Bell and Murphy's figures.

In conclusion, it appears from the phase-rule studies at 25° and 100° that the only basic sulphate of copper which has any real claim to be regarded as a "compound" at these temperatures is $4CuO,SO_3,4H_2O$. There is much evidence for the belief that the same statement holds for intermediate temperatures.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, August* 16*th*, 1926.]