

free from bismuth and antimony, the method can be materially shortened. Instead of bringing the ore into solution with a mixture of nitric and sulphuric acids, nitric acid alone is used. After solution, the acid is neutralized with an excess of ammonia and then made acid with acetic acid; this dissolves any lead sulphate that has been formed. This solution is then immediately titrated with the bichromate and ammonio ferrous sulphate solutions exactly as described above. The following table shows the agreement in the results obtained by this method :

No.	Weight taken. Grams.	Calculated weight lead found. Grams.	Lead per cent.
1	0.9983	0.8570	85.84
2	0.9987	0.8578	85.82
3	0.9997	0.8588	86.08
4	0.9806	0.8421	85.88
5	0.9996	0.8570	85.72
6	0.9971	0.8558	85.84
7	0.9975	0.8580	86.02
8	0.9936	0.8533	85.90

In general it may be said that the results are a trifle low. The mean of the amount of lead recovered in twenty determinations carried out by one of us was 99.6 per cent. of that taken.

We do not know that the modification as used by us has never before been tried, but our results appeared to possess sufficient value to warrant publication.

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REACTIONS BETWEEN COPPER AND CONCENTRATED SULPHURIC ACID,¹

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Received September 9, 1895.

ANDREWS² in writing on the "Assumption of a Special Nascent State," argued that the production of sulphur dioxide, as a result of the reaction between copper and concentrated sulphuric acid, was due not to nascent hydrogen, as is commonly considered, but to the deoxidation of sulphur trioxide by the copper with the production of copper oxide as a primary pro-

¹ Read at the Springfield meeting.

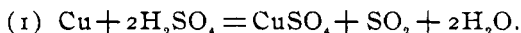
² Chem. News, 70, 152.; Iowa Acad. of Sciences, Proc. p. 4.

duct. Having noted frequently the evolution of sulphur dioxide gas before any evidence of this "copper oxide," at the suggestion of Dr. F. P. Venable, I began some experiments with a view of studying this complicated reaction so simply treated in most text-books.

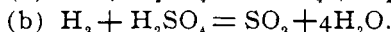
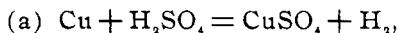
When my work was completed, in verifying my references I chanced on Pickering's¹ work on the same subject which had escaped me. Most of my work, especially that part which concerns the secondary reactions, is in accord with that of Prof. Pickering. My observations concerning the primary reactions were not the same however. In making known the latter, I feel at liberty to give the results of my work, as independent corroboration is of some value.

The reactions which take place when copper is treated with concentrated sulphuric acid may be divided into primary and secondary.

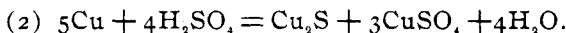
Primary:



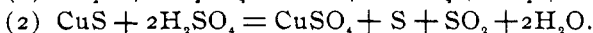
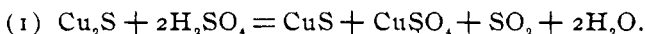
This may be regarded as taking place in two steps:



Still no hydrogen could be detected in the gas given off.



Secondary:



The experiments were carried out under various conditions of temperature and time, exposure of the metal to the action of the acid, and varying proportions of metal and acid. The copper ribbon used was cut into small pieces one cm. wide by two to three cm. long. Concentrated C. P. sulphuric acid, 1.84 sp. gr. was used. Each experiment, except where noted, was carried out in a flask in which the air had been displaced by a neutral gas, hydrogen or carbon dioxide. The evolved sulphur dioxide was led through a strong solution of sodium hydroxide

¹ J. Lond. Chem. Soc. Trans., 1878, p. 112.

and the sulphite formed titrated with a standard iodine solution or oxidized by bromine, and the sulphuric acid determined gravimetrically. A rapid stream of the inert gas was driven through the apparatus just at the close of the experiment. Water was poured into the flask and the whole quickly filtered, and the copper remaining unattacked was then cleaned as well as possible by rubbing, dried and weighed. The copper as sulphate was determined by electrolysis. The residue was burned in a porcelain crucible, treated with concentrated nitric acid, ignited and weighed as copper oxide. Sulphur was determined by weighing a dried portion of the residue treating with carbon disulphide and the loss in weight taken as sulphur.

Primary Reactions.—My experiments showed that the first of the primary reactions predominated when copper was treated with concentrated sulphuric acid at different temperatures (0° – 270° C.) At the highest temperature it was found that that reaction alone took place, but at all lower temperatures the second primary reaction also occurred. The proportion of the material following the second equation increased from 0° to 100° C., and then decreased to 270° C., when there was no longer evidence of any such reaction, that is, no black residue was formed.

At the lower temperatures, under 100° C., only the two primary reactions seemed to take place; at the higher temperatures the secondary reactions if the action were prolonged, frequently set in, complicating matters as far as quantitative determinations were concerned. If the time of action were shortened evidence of the occurrence of the primary reactions alone was found. Having an excess of copper present was also necessary, because as soon as all the copper had been attacked the secondary reactions set in at once.

The conditions seemed most favorable for the formation of the insoluble residue at the temperatures from 100° to 130° C. as may be seen from the table. The proportion of the insoluble residue decreases rapidly in either direction from these temperatures. Some insoluble residue is produced at all the lower temperatures but none is produced when the reaction takes place at 270° C. and lasts for only a few seconds.

No.	Temperature of reaction.	Copper used.	Copper as sulphate.	Copper as sulphide.	Sulphur dioxide produced.	Ratio of copper sulphate to copper sulphide.
1	0°-10°	0.1350	0.1340	0.0005	0.1343	268.0 : 1
2	"	0.0750	0.0740	0.0003	0.0780	246.0 : 1
3	20°-30°	1.3379	1.3260	0.0121	118.9 : 1
4	"	1.2473	1.2000	0.0184	1.2442	68.0 : 1
5	65°	0.1650	0.1600	0.0050	0.1648	33.0 : 1
6	70°-80°	0.0760	0.0730	0.0035	21.0 : 1
7	100°	0.1380	0.1060	0.0300	0.0840	3.5 : 2
8	"	0.3818	0.2800	0.1082	0.1166	3.5 : 1
9	"	0.9200	0.6400	0.2748	0.2165	3.3 : 1
10	120°-130°	5.2578	4.0800	1.1946	2.0932	3.5 : 1
11	140°-160°	5.0900	4.5100	0.5759	3.3084	8.0 : 1
12	160°-190°	1.1375	1.1200	0.0930	12.0 : 1
13	200°-220°	1.5450	1.4518	0.0932	1.0904	16.0 : 1
14	220°-230°	0.9815	0.9400	0.0332	0.9365	29.0 : 1
15	230°	3.8915	3.8200	0.0796	3.6327	49.0 : 1
16	230°	2.0000	1.9750	0.0388	2.2313	51.0 : 1
17	240°	1.1235	1.1035	0.0200	0.9855	55.0 : 1
18	250°-260°	2.1365	2.1000	0.0280	2.0304	80.0 : 1
19	270°	4.0000	None.

Berzelius¹ noted this black substance when copper was treated with concentrated sulphuric acid. He said it appeared to be a subsulphate because it was oxidizable by nitric acid. He made no quantitative determinations to show its composition. Such a body would contain fifty-seven per cent. of copper and in no case did I find the black residue to contain less than 67.64 per cent.

Barruel² found that sulphuric acid acted on copper at ordinary temperatures if sufficient time were given. He claimed that the sulphur dioxide produced was dissolved in the acid and attacked the copper forming copper sulphide and oxide, the latter being dissolved in the acid.

Mauméné³ claimed that his black residue contained four different bodies; copper subsulphide and three oxysulphides, $\text{CuO} \cdot 2\text{Cu}_2\text{S}$ or $\text{Cu}_5\text{S}_2\text{O}_7$, $\text{CuO} \cdot 2\text{CuS}$ or $\text{Cu}_3\text{S}_2\text{O}_7$, and $\text{CuO} \cdot \text{CuS}$ or Cu_2SO .

In my analyses, as also in Pickering's, the sum of the percent-

¹ *Traité de chimie*, 4, 324.

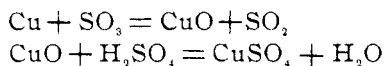
² *Journ. de Pharm.* 20, 13, 1834.

³ *Ann. Chim. Phys.*, 1846, 3rd Series, 18, 311; *Traité de chimie générale*, Pelouze et Fremy, 2nd Ed., I 388.

ages of copper and sulphur always approximated 100. In one experiment I did find a body whose composition approximated $\text{CuO}_2\text{Cu}_2\text{S}$. I shall speak of that apparent exception further on.

Calvert and Johnson¹ performed some experiments on the action of strong and dilute sulphuric acid on copper at temperatures from 130° to 150° C. They noted the formation of the sub-sulphide and claimed it was due to the liberation of free sulphur which afterwards combined with the copper direct.² There was evidently something very wrong in their observations, for they failed to note any action below 130° C. Barruel in 1834 had noted that action took place at the temperature of the air. I have noted the action at 0° C.

According to Andrews

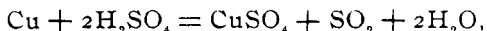


are the correct formulas, SO_3 existing at the temperature necessary for the reaction, and the insoluble residue being the oxide. That would do if the reaction occurred only at those higher temperatures, whereas it occurs as well at 0° C. Besides this the undissolved residue is not the oxide at all, as he says it is, but invariably the sulphide. In making his analyses very likely he determined the copper alone and the percentage of copper in copper oxide and cuprous sulphide is the same. In a subsequent conversation with Dr. Andrews, I have learned that this was the case. This black residue when thoroughly washed free from any sulphuric acid always gave off hydrogen sulphide on treatment with hydrochloric acid.

The composition of the insoluble residue was determined by analysis:

	Found.	Calculated for Cu_2S .
Sulphur.....	20.44	20.14
Copper.....	79.56	79.86
	<hr/> 100.00	<hr/> 100.00

In the first of the two primary reactions,



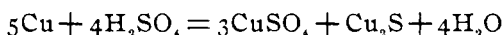
¹ J. Chem. Soc., 19, 438, 1866.

² Pickering proved this impossible. The amount of sulphide produced was not increased by adding sulphur direct to the experiment.

it is seen that for each atom of copper found as sulphate, one molecule of sulphur dioxide should be evolved: Calculating on this basis from the following table we have the ratio of 2 : 3 between the copper as subsulphide and the copper as sulphate unaccounted for in the production of the sulphur dioxide.

No.	Sulphur dioxide.	Corresponding copper.	Total copper as sulphate.	Copper as sulphide.	Difference. Columns 3 and 4.	Ratio. Columns 5 and 6.
8	0.1166	0.1158	0.2800	0.1082	0.1642	2 : 3
9	0.2165	0.2132	0.6400	0.2758	0.4268	2 : 3

The formula



shows that relation between the two compounds of copper.¹

Secondary Reactions.—The secondary reactions depend upon the second of the primary, that is, the cuprous sulphide produced. If the experiment were carried out so as to cause a rapid evolution of gas and the residue not allowed to form a protective coating over the copper, as long as an excess of the metal was present, only the primary reactions occurred. This was accomplished at 160°–170° C. If the strips of copper were touching they almost always became bound together by the anhydrous copper sulphate and a coating of the black residue formed a protective covering to the copper. When such a state of affairs occurred, no sharply defined line could be drawn to show, of these secondary reactions, when the first ends and the second begins, because as soon as some cuprous sulphide is changed to cupric sulphide, the latter is attacked by the sulphuric acid, sulphur being one of the products of the last reaction. Several experiments carried out at 140°–150° C when this occurred with an excess of copper gave evidence of all the reactions, primary and secondary. Sulphur was deposited on the sides of the flask and the black residue contained 20.71 per cent. sulphur, and the theoretical percentage for cuprous sulphide is 20.138. This showed the presence of some cupric sulphide in which the percentage of sulphur is 33.59.²

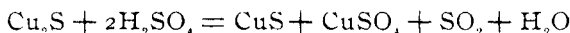
¹ Pickering states (*loc. cit.*, p 117) that once at 80° C. he observed that the copper in the two compounds stood in the relation of 2 : 2.9. I have not been able, however, to have concentrated sulphuric acid act on copper at any temperature from 0° C. to 270° C. without the evolution of sulphur dioxide, which is not accounted for at all in case the second of the primary reactions alone takes place, which he states did take place at 80° C.

² Watts (vol. II, p. 41, 1875, Ed.) notes this complete decomposition.

Some freshly prepared cuprous sulphide was treated with concentrated sulphuric acid. Sulphur was determined in the undissolved residue, the free sulphur being first removed.

	Found.	Calculated for CuS.
Sulphur	32.36	33.59

The formula,

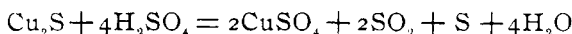


explains such a change.

Another portion of cuprous sulphide was boiled with concentrated acid until it nearly all disappeared. The free sulphur produced was determined.

	Found.	Calculated.
Sulphur	19.71	20.138

The formula



shows the final result of the continued action of sulphuric acid on the subsulphide.

From these data the secondary reactions between copper and concentrated sulphuric acid may be expressed by the two formulas,

1. $\text{Cu}_2\text{S} + 2\text{H}_2\text{SO}_4 = \text{CuS} + \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}.$
2. $\text{CuS} + 2\text{H}_2\text{SO}_4 = \text{S} + \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}.$

The occurrence of sulphur on the sides of the flask at the end of the reaction may be said to be due to the sublimation of that element which is produced by the direct decomposition of sulphuric acid without the intermediate formation of hydrogen sulphide for the following reasons :

1. If hydrogen sulphide were produced by the decomposition of the sulphide, it is natural to expect some to escape in the gases which are given off. None could be detected.
2. As is well known, hydrogen sulphide is decomposed by concentrated sulphuric acid.
3. The deposit of sulphur is first noted on the sides of the flask and not in the delivery tube where the gases, hydrogen sulphide, and sulphur dioxide, would naturally come into the most intimate relations.
4. If flowers of sulphur be heated with concentrated sulphuric

acid in a flask provided with a long outlet tube, much of the sulphur will be seen to creep up the sides of the flask, and some sublimed even into the tube, which shows that the state of affairs observed may be attained without any trace of hydrogen sulphide being present.

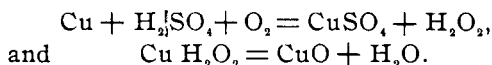
COPPER OXYSULPHIDE.

Contradictory evidence to what has been stated above was found in one case where the insoluble residue approximated $\text{CuO} \cdot 2\text{Cu}_2\text{S}$ in composition. This is one of the oxysulphides stated by Maumené to exist in the black residue. The acid was heated to 250°C . in an Erlenmeyer flask. The air was not removed by an inert gas. The copper was suspended in long strips, only a third of which was immersed in the acid, the other part being exposed to the air.

The black residue formed under these conditions gave on analysis :

	Found.	Calculated for $\text{CuO} \cdot 2\text{Cu}_2\text{S}$.
Sulphur	16.16	16.15
Oxygen	3.54	4.03
Copper	undetermined	79.82

Schuster¹ found that copper was acted on by dilute sulphuric acid only in the presence of atmospheric oxygen. Traube² noted that copper was not oxidized in moist air, but was slowly in the presence of dilute sulphuric acid. Although copper is unable to decompose sulphuric acid at ordinary temperatures (according to Traube) its affinity for SO_4 and that of hydrogen for oxygen are together sufficient to cause such a decomposition, the probable reaction being :



I could detect no oxygen in the gases given off when the experiments were carried out in an inert atmosphere. Nor could I detect hydrogen peroxide. Traube himself states that no "active" oxygen was liberated in the reaction because carbon monoxide was not oxidized to carbon dioxide. Pickering³ sug-

¹ Proc. Roy. Soc., 55, 84; *Ber. d. chem. Ges.*, 28, 219.

² *Ber. d. chem. Ges.*, 18, 1887-1890.

³ *Loc. cit.*, p. 138.

gests that the sulphide formed is "oxidized at the time of its appearance by the oxygen which would be liberated at the surface of that portion of the copper which is immersed in the acid, since the whole arrangement would form a galvanic cell consisting of a metal, a liquid, and a gas."

UNIVERSITY OF NORTH CAROLINA.

NEW BOOKS.

PRINCIPLES AND PRACTICE OF AGRICULTURAL ANALYSIS. BY HARVEY W. WILEY. Volume I, Soils. Cloth, 8 vo., pp. 607, figures, 93. Easton: Chemical Publishing Co. 1894. Price, \$3.75.

This first bound volume includes the first eight parts of the compendious work now in process of publication.

In attempting to meet the wants alike of analysts, teachers, and students of agricultural chemistry, the author has undertaken a most difficult task. The needs of the several classes of readers are widely different, often distinctly opposite.

Beyond doubt, each of the classes named has need of a thoroughly modern treatise upon this subject. There is extant no satisfactory systematic introduction through the general principles of analysis to the special methods applicable to agricultural materials; the student is ordinarily compelled to the study of many methods, in the illustration of general principles and for the acquirement of facility in manipulation, that are not directly required in his future work, and which might often be happily substituted by methods which are of immediate use. Again, there is no English work on agricultural analysis—except of the most incomplete scope—which is at all modern; nor does any work upon the subject in any language cover the methods developed in America during the past ten years. On the other side, the Proceedings of the Association of Official Agricultural Chemists state the American official methods most briefly, for the guidance of analysts presumably acquainted with the methods in general, and more or less familiar with the reasons for the several specifications, and, therefore, without explanatory comment; nor has this Association undertaken, as yet, to cover all of the large field involved. Even assuming a degree of linguistic attainment altogether beyond that of the average student, and of