$$2S_R = S_2\,(g);\ \Delta F^\circ = 29600 + 1.74T\ln T + 0.0042T^2 - 51.3T, \quad (13)$$

and

$$\Delta F^\circ_{298} = 17600.$$

We wish to express our obligation to the Rumford Fund of the American Academy of Arts and Sciences for financial aid in this investigation.

Summary.

The following table gives the free energy of formation of the forms of sulfur considered in this paper:

TABLE II.

Substance.	F°_{298}.	Equation.	Substance.	F°_{298}.	Equation.
S_R	0	..	$S_{\lambda,\mu}$	—0.8	(Table I)
S_M	17.5	5	S_2	17600	13
S_λ	94	9			

BERKELEY, CAL.

DETERMINATION OF CUPROUS AND CUPRIC SULFIDE IN MIXTURES OF ONE ANOTHER.

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In the course of an investigation upon copper sulfide minerals, which at the present time is being carried out in this laboratory, it became necessary to discover a method to determine cuprous and cupric sulfide in their mixtures. Such a determination involves great difficulties for the reason that no solvents are known for either of them, *i. e.*, solvents which dissolve them without decomposition. It was therefore necessary to find a substance that would react with only one of the components, or, if reacting with both of them, would yield with each of them a different substance, which in turn could in some way be easily separated and determined.

Several reactions were tried, for instance the oxidation of cuprous sulfide. It is well known that cuprous sulfide changes in an acid solution in the presence of oxygen into cupric sulfide. But experiments showed that this reaction did not stop at cupric sulfide, and that cupric sulfide was also much attacked under these conditions. Finally it was found that the reaction of cuprous and cupric sulfide with silver nitrate offered, under certain conditions, a method for their determination.

The reaction between cuprous sulfide and silver salts has been examined by Heumann,[1] Schneider[2] and more recently by C. Palmer and E. S. Bastin.[3] As a result, this reaction has been expressed by the equation

$$Cu_2S + 2Ag_2SO_4 = Ag_2S + 2Ag + 2CuSO_4$$

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[1] *Ber.*, **7**, 1680 (1874).

[2] *Pogg. Ann. Physik.*, **152**, 471 (1874).

[3] *Economic Geology*, **8**, 140 (1913).

Regarding the reaction between cupric sulfide and silver salts Anthon[1] and Schuermann[2] report the formation of silver sulfide; whereas C. Palmer and E. S. Bastin[3] assert that metallic silver as well as silver sulfide is formed. It was therefore necessary to determine this reaction.

A very pure specimen of covellite from Butte, Montana (Cu 66.43%, S 33.28%, Fe 0.05%, SiO_2 0.07%), and a chemically pure synthetic cupric sulfide were used. The very finely ground material was heated for several hours on the steam bath with solutions of silver nitrate and sulfate, respectively. The resulting substance was then filtered and washed. It proved to be silver sulfide. Dr. H. E. Merwin kindly examined it microscopically. He found it to be perfectly homogeneous and in neither case when natural or synthetic cupric sulfide was used, could he detect any metallic silver.

Substances resulting from the reaction of the silver salt upon cupric sulfide were analyzed. The results are given in Table I.

TABLE I.

Weight of cupric sulfide in g.	Silver found in the resulting substance.	Mol silver for each mol of cupric sulfide.	Remarks.
0.3178	0.7216	2.01	Synthetic CuS treated with Ag_2SO_4
0.3184	0.7169	1.99	Synthetic CuS treated with $AgNO_3$
0.3164	0.7029	1.98	Natural CuS (Butte, Montana) treated with $AgNO_3$

One may see from this table that synthetic cupric sulfide acts exactly like the natural mineral and that the nature of the silver salt has no specific influence on the reaction. Further, that, when the reaction between cupric sulfide and silver salt solution takes place, each mol of cupric sulfide reacts with two mols of silver, as is necessary for the formation of silver sulfide. The reaction may therefore be written

$$CuS + 2AgNO_3 = Ag_2S + Cu(NO_3)_2$$

It was also shown in a different way that no metallic silver is formed by the reaction between cupric sulfide and silver nitrate, while the reaction between cuprous sulfide and silver nitrate gives equal quantities of silver, as metallic silver and as silver sulfide.

It is known that metallic silver can be dissolved in a solution of ferric nitrate. This reaction may be expressed as follows:[4]

$$Ag + Fe(NO_3)_3 \rightleftarrows AgNO_3 + Fe(NO_3)_2$$

According to the thermochemical equation[5]

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[1] *J. prakt. Chem.*, **10**, 355 (1837).

[2] *Ann.*, **249**, 326.

[3] *Loc. cit.*

[4] THIS JOURNAL, **34**, 1016 (1912).

[5] Landolt-Börnstein-Roth Tabellen.

$$Ag + Fe(NO_3)_3.Aq = AgNO_3.Aq + Fe(NO_3)_2.Aq - 172{,}300 \text{ cal.}$$

the equilibrium will be displaced from left to right with increase of temperature. An excess of ferric nitrate will also displace the equilibrium in the same direction, so that conditions are readily found, under which practically all the silver may be dissolved. It was found that a 6% solution of ferric nitrate (anhydrous) and a temperature of about 70° were well adapted to this purpose.

The substances resulting from the reaction of cuprous and cupric sulfide, respectively, with silver nitrate were now tested for the quantity of metallic silver they contained. Each was treated twice with the solution of ferric nitrate and filtered through a hot water funnel. The silver was then determined in the solution as well as in the residue. The results are given in Table II.

TABLE II.

Weight of original substance.	Silver extracted with ferric nitrate solution.	Silver in the residue.	Ratio of extracted silver to the silver in the residue.
0.3188 g. Cu_2S	0.4263	0.4292	0.993
0.3226 g. CuS	0.0096	0.7170	0.013

The last column in this table gives the ratio of silver found in the ferric nitrate extract to the silver found in the residue. It shows that in the case of cuprous sulfide this ratio, within the limits of the experimental error, is 1. This means that the substance resulting from the treatment of cuprous sulfide with silver nitrate contains equal amounts of silver as metallic silver and as silver sulfide, and confirms the above reaction, *viz.*,

$$Cu_2S + 4AgNO_3 = Ag_2S + 2Ag + 2Cu(NO_3)_2.$$

Treating the substance resulting from the reaction of cupric sulfide and silver nitrate with ferric nitrate, a small amount of silver was found in the extract as shown in the table. This amount (1.3% of the total silver) lies probably within the experimental errors and might be due to some decomposition of silver sulfide. This together with the previous experiments on this point, proves that no metallic silver was present and we can express the reaction between cupric sulfide and silver nitrate by the equation

$$CuS + 2AgNO_3 = Ag_2S + Cu(NO_3)_2$$

The different ways in which cuprous and cupric sulfide react with silver nitrate give us the possibility of determining each of them in a mixture of the two. After treating such a mixture with silver nitrate it would only be necessary to separate, in the resulting substance, the metallic silver from the silver sulfide, which we have previously seen can be accomplished by means of a ferric nitrate solution. The silver is then determined in the filtrate as well as in the residue. The amount of cuprous sulfide is calculated from the silver found in the filtrate. The difference in silver found in the residue and in the filtrate serves for the calculation of the cupric sulfide. For, if the substance consisted only of cuprous sulfide we should find equal quantities of silver in the filtrate and in the residue (within the limit of experimental error), while if cupric sulfide was present, there would be more silver in the residue than in the filtrate and this excess would correspond to the amount of cupric sulfide in the mixture.

To make such a determination, conditions described below must be followed. The substance to be examined must be at least fine enough to pass through a 200 mesh (per linear inch) sieve. About 0.4–0.5 g. material are treated with 50 cc. of a 5% silver nitrate solution, which is added gradually with vigorous stirring. Most of the reaction takes place within a few minutes. To complete it, however, the covered beaker must be put on the steam bath for about 3 hrs. and the contents vigorously stirred at short intervals. The stirring is necessary because some of the material might otherwise be enveloped with metallic silver and silver sulfide and this small quantity might remain unchanged. After the reaction is complete the precipitate is filtered and washed by decantation till the filtrate no longer reacts with hydrochloric acid. The precipitate is then collected in the beaker and extracted two or three times with 40–50 cc. of a 6% solution of ferric nitrate (anhydrous). This operation is carried out at about 70°.[1] The extract is filtered each time through a hot

TABLE III.

	Original mixture in per cent.	Ratio found in per cent.	Difference.
Cu_2S	96.25	96.36	±0.11
CuS	3.75	3.64	
Cu_2S	93.80	92.50	∓1.30
CuS	6.20	7.50	
Cu_2S	93.06	91.50	∓1.56
CuS	6.94	8.50	
Cu_2S	84.76	83.70	∓1.06
CuS	15.24	16.30	
Cu_2S	79.08	77.60	∓1.48
CuS	20.92	22.40	
Cu_2S	45.07	45.36	±0.29
CuS	54.93	54.64	
Cu_2S	12.35	12.64	±0.29
CuS	87.65	87.36	
Cu_2S	10.43	10.31	∓0.12
CuS	89.57	89.69	
Cu_2S	4.95	5.39	±0.44
CuS	95.05	94.61	
Cu_2S	1.66	2.96	±1.30
CuS	98.34	97.04	

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[1] Higher temperature causes hydrolysis and precipitation.

water funnel and the residue is finally washed with hot water. To the filtrate nitric acid is then added until it becomes colorless. The silver is then precipitated and weighed as silver chloride. The residue is roasted, dissolved in nitric acid and the silver determined as silver chloride. The percentage of cuprous and cupric sulfide in the mixture is calculated from the quantities of silver chloride. Table III gives a number of such determinations. They were made with natural cuprous (Cu 79.67%, S 20.16%, Fe 0.14%, SiO_2 0.06%) and cupric sulfides (given above).

As seen from these results the method is accurate within 1.5%, which may be regarded as satisfactory.

In this method the metallic silver alone may be determined and from this, if the original weight of the substance is known, both cuprous and cupric sulfide may be calculated. However, the assumption that the silver found is strictly proportional to the quantity of cuprous sulfide is not safe. It sometimes happens that, owing to insufficient stirring, a small part of the mixture (Cu_2S, CuS) does not react with silver nitrate. The absolute amount of cuprous sulfide that corresponds to the metallic silver would in such case be too low. But the occlusion probably affects cupric sulfide in a similar degree as it does cuprous sulfide. For that reason if both were determined, both would be too low while their percentages, calculated from the total weight found, would be correct. The data given in the last table under "found" were calculated in this way.

Summary.

The reaction between cuprous sulfide and silver nitrate was confirmed in accordance with the equation:

$$Cu_2S + 4AgNO_3 = Ag_2S + 2Ag + 2Cu(NO_3)_2$$

It was found that silver sulfide only, and no metallic silver, is formed by the reaction between cupric sulfide and silver nitrate, the equation for this reaction being

$$CuS + 2AgNO_3 = Ag_2S + Cu(NO_3)_2$$

Based on the difference between these reactions a method is given for the determination of cuprous and cupric sulfide in mixtures of the two. The mixture is treated with silver nitrate and from the product the metallic silver is extracted by means of ferric nitrate. The amount of cuprous sulfide is calculated from the metallic silver, while the cupric sulfide is calculated from the difference between the silver in the silver sulfide and the metallic silver.

In mixtures containing the constituents in any proportion whatever the method was shown to be accurate within 1.5%.

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