

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SYRACUSE UNIVERSITY.]

## POLYMORPHIC TRANSFORMATIONS OF ANTIMONY TRISULFIDE.

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Between 1878 and 1890 several researches<sup>1,2</sup> on the transformation of the red anhydrous and the orange hydrated forms of antimony trisulfide into the black variety were performed. Those of Ditte<sup>3</sup> and Lang<sup>4</sup> were most significant, but neither investigator worked under rigorously controlled conditions. Lang used aqueous hydrochloric acid at room temperature and found that the time required for transformation of the red form to the black varied inversely with the concentration of the acid employed, ranging from 8 days for a 22% to 150 days for a 1% solution. Ditte worked with the orange-red dihydrate, using excess of acid and high temperatures.

A more quantitative study of this transformation appeared to us desirable. Accordingly the red sulfide was prepared by precipitation with washed hydrogen sulfide from a dil. tartar emetic solution acidified with tartaric acid. The precipitate was washed in succession with water, potassium carbonate solution, water, tartaric acid solution, water, alcohol, carbon disulfide and ether, then dried at 110°. The brick-red amorphous sulfide thus obtained was powdered and passed through a 40-mesh screen,

The first series of experiments was carried on with 2g. samples of the sulfide in small flasks. Five-cc. portions of the reagent were added, the flask stoppered and examined at regular intervals to note whether a change to the black form had occurred. The temperature ranged from 18° to 22°. As reagents hydrochloric acid of 1 *N*, 7 *N*, and 12 *N* concentrations, 7 *N* phosphoric acid; 7 *N* sulfuric acid; glacial and 1 *N* acetic acid, and an ether solution saturated with dry hydrogen chloride were employed. Of these, only the hydrochloric acid solutions in water gave any appreciable transformation, even after the lapse of two months. The time required for these was much less than for those found by Lang. For 12 *N*, 7 *N* and 1 *N* hydrochloric acid, the time required for transformation was 0.5 day, 1 day and 10.5 days, respectively.

Time measurements in all cases were made to the point of final transformation, that is, until no more red particles could be seen. At lower temperatures the transformation is gradual, the finer particles changing first, but it speeds up towards the end, and at higher temperatures is so rapid that the eye can scarcely measure the time interval between incipient and final transformation.

<sup>1</sup> Clermont and Frommel, *Compt. rend.*, **86**, 87 (1878).

<sup>2</sup> Scheuerman, *Ann.*, **249**, 339 (1888).

<sup>3</sup> Ditte, *Compt. rend.*, **102**, 212 (1886).

<sup>4</sup> Lang, *Ber.*, **18**, 2716 (1885).

The difference between the above results and those of Lang may be due in part to the greater fineness of our particles, but it is more probably explained by the fact that Lang permitted the evolved hydrogen sulfide to escape, thus constantly displacing the equilibrium, whereas in these experiments all the flasks were carefully stoppered.

The action is due, apparently, to a solution of the red sulfide in the acid, followed by a reprecipitation of the less soluble black modification. These black crystals under the microscope showed the characteristic orthorhombic faces of the mineral stibnite.

Further experiments were made to determine the effect of temperature on the velocity of transformation. A 20% hydrochloric acid solution was used, with the same proportions of acid and red sulfide as before. The experiments were carried out in a thermostat at a series of temperatures up to 75° with a maximum variation of 0.5°; 25cm. test-tubes were used instead of flasks.

Temperature. °C.	Time required.	
	Hrs.	Min.
26.5	44	..
30	29	..
35	16	..
40	9	..
68.5	..	62
75	..	32

The very rapid increase of speed of transformation with rise of temperature is noteworthy.

Under similar conditions, a 20% solution of hydrobromic acid gave no visible blackening, even after 20 hours at 75°.

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## THE REDUCTION OF COPPER OXIDE BY HYDROGEN.

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This investigation of the reduction of copper oxide by hydrogen was undertaken in the hope that the results might throw some light on the mechanism of the catalytic combination of hydrogen and oxygen in the presence of metallic copper, in a study of which we have been engaged.<sup>1</sup> Since copper oxide may be reduced by hydrogen and the resulting copper may be re-oxidized without difficulty at temperatures at which the metal is catalytically active, it would appear that, in all probability, the catalytic reaction proceeded as a result of the alternate oxidation and reduction of the copper. Certain of our results were apparently inconsistent

<sup>1</sup> The results of this investigation will be published shortly.