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## The Reduction of Sulphuric Acid by Copper as a Function of the Temperature

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## THE REDUCTION OF SULPHURIC ACID BY COPPER AS A FUNCTION OF THE TEMPERATURE.

LAUNCELOT W. ANDREWS.

The object of the experiments described in this paper was to determine whether the reduction of sulphuric to sulphurous acid by copper takes place at a lower or at a higher temperature than the incipient dissociation of the former compound into water and the acid anhydride.

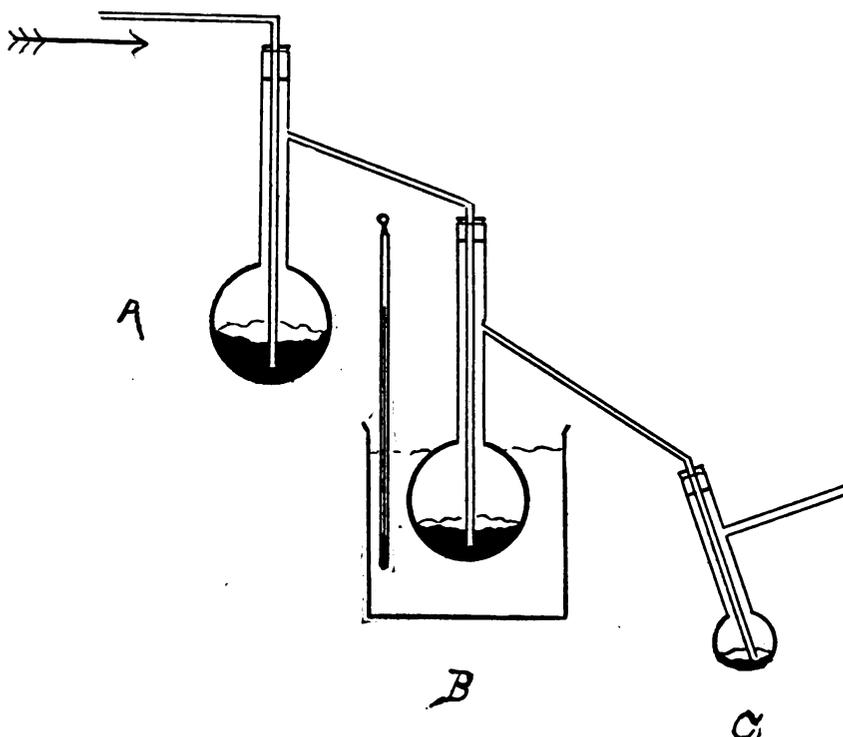


FIGURE 1.

The sulphuric acid employed was the ordinary pure product, containing 98.4 per cent of  $H_2SO_4$ . The apparatus illustrated in the figure was used.

The method employed was to heat the copper with the sulphuric acid (in flask B) gradually in a sulphuric acid bath while

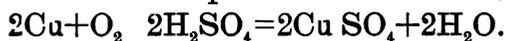
passing a dry current of air or of carbonic anhydride through it. The escaping gas was then tested (in flask C) by suitable reagents, to be described, for sulphuric and sulphurous anhydrides respectively. Flask A contained concentrated sulphuric acid of the ordinary temperature (25°C) to dry the gas, which was usually passed at the rate of about eighty bubbles per minute. The importance of securing absence of dust from the acid being recognized, the interior of the whole apparatus was washed with boiling concentrated sulphuric acid and dried in dustless air.

*Experiment I.*—Flasks A and B were charged with concentrated sulphuric acid and C with a solution of barium chloride. Air was drawn through the whole in a slow current for fifteen minutes. The solution in C remained clear. B was now very slowly heated while the current of air was maintained.

Before the bath reached 70°C there appeared in C a faint turbidity of barium sulphate, which at the temperature named became distinct. At 60°C the solution remained unchanged, even after passing the air for a long time. Hence sulphuric acid of the given concentration begins to give up sulphuric anhydrides, that is, it begins to dissociate at a temperature lying between 60° and 70°C.

*Experiment II.*—The apparatus charged as before, with the addition of pure bright copper wire in B, and with highly dilute iodide of starch instead of barium chloride in C. After passing air for several hours at the ordinary temperature, much of the copper had gone into solution and anhydrous copper sulphate had begun to crystallize out, but the iodide of starch, made originally very pale blue, retained its color.

This shows that in the presence of air, sulphuric acid is attacked by copper at ordinary temperatures, but without reduction of the acid. The reaction must take place in accordance with the equation:



*Experiment III.*—This was like the last, except that the apparatus was filled with carbonic anhydride, and a current of this gas was substituted for air.

The copper was not attacked, and the starch iodide was not decolorized. The temperature of B was now slowly raised, and when it reached 90° the solution in C was bleached. In a similar experiment a solution of dilute sulphuric acid, colored pale straw with potassium bichromate, was used as an indicator for

sulphurous acid in C. In this case the change of color did not occur until the temperature had risen to  $108^{\circ}$ , the indicator being, as might be expected, less sensitive than the other.

*Experiment IV.*—Same as III, except that a reagent for both sulphuric and sulphurous acid was used in C.

This reagent was prepared by slightly acidifying a solution of barium chloride with hydrochloric acid and then adding enough potassium permanganate to render the solution pale rose color.

This indicator is capable of showing the presence of considerably less than  $\frac{1}{100}$  m. g. of sulphurous acid.

When the temperature of the bath had reached  $70^{\circ}\text{C}$  the solution in C was distinctly turbid with barium sulphate, but its color was unaltered. At  $86^{\circ}$  it began rather suddenly to bleach, and at  $87^{\circ}$  it was colorless. Special care was taken in filling B not to get any sulphuric acid on the neck or sides of the flask. A repetition of this experiment gave identical results, the gas being passed at the rate of two to three bubbles per second.

The conclusions to be drawn from this investigation are:

*First.*—That the dissociation of sulphuric acid of 98.4 per cent. begins to be appreciable at a temperature somewhat below  $70^{\circ}$ , which may be estimated at about  $67^{\circ}$ .

*Second.*—The reduction of sulphuric acid by copper does not begin below  $86^{\circ}$ , that is, not until the acid contains free anhydride.

The assertion made by Baskerville,<sup>1</sup> that sulphuric acid is reduced by copper at  $0^{\circ}$  is, therefore, incorrect. He appears to have based the statement, not on any demonstration of the formation of sulphurous acid, but solely on the formation of copper sulphate, which occurs, as I have shown,<sup>2</sup> in consequence of the presence of air.

A more careful repetition of his experiments under conditions securing entire exclusion of air can but lead him to a different conclusion from that he obtained at first.

The fact adduced by him that under certain conditions cuprous sulphide may be formed by the action of the metal upon sulphuric acid does not allow any conclusions to be drawn respecting the presence of "nascent" hydrogen, since it may be explained perfectly well either by the direct reducing action

<sup>1</sup>Journal of the Am. Chem. Soc., 1895, 908.

<sup>2</sup>Traube has shown the same thing for dilute sulphuric acid. *Ber.* 18, 1888.

of the copper or by Traube's theory which is backed up by almost convincing evidence<sup>3</sup>.

Stannous chloride will reduce sulphuric acid with formation of hydrogen sulphide and free sulphur, an analogous reaction in which the assumption of "nascent" hydrogen is inadmissible.

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<sup>3</sup>Moritz Traube, *loc. cit.* and *Ber.*, 18, 1877, etc.

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## CLAYS OF THE INDIANOLA BRICK, TILE AND POTTERY WORKS

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L. A. YOUTZ, INDIANOLA.

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Analyses of several clays from a brickyard at Indianola have recently been made by me to go into a report of the Geological Survey of Warren county. Though it has been said that a knowledge of the constituents of a clay, determined by a purely chemical analysis, is of very little value to a practical brick-maker, yet in comparing the analyses of these clays and those from other vicinities, it seems that points of great value to the manufacturer are made plain, and points that can be derived from no other source. So I wish to give a few ideas which came to me as I made the comparison, as points, of local interest at least, were, it seems to me, clearly brought out.

In order to get an intelligent idea of the value of this clay for brick and tile it may be helpful to give a short outline of some of the qualities of clay for the various kinds of brick. The quality and character of brick depends, of course, primarily upon the kinds of earth used; the mechanical mixing, drying and burning being important items, however.

The varieties of clay most frequently used for common bricks are three. The so-called blue clays, hydrated aluminum silicates, combined with small quantities of iron, calcium, magnesium and alkalis; sandy clays or loams, and marls which contain a large proportion of lime and magnesium. In addition to these are the clays for special kinds of brick, as fire-brick, pottery, terra cotta, etc. Hydrated silicate of aluminum is infusible even at the most intense furnace heat, but if these be mixed with alkalis, or alkali earths, it becomes fusible, and in