

a time without decomposition or loss in any way. The residue by evaporation of this solution, in air, or hydrogen, or vacuum, contains a considerable portion of the unchanged hydroxide, along with certain decomposition products not yet determined. The normal carbonate of this base, its normal sulphate, and its platinum chloride are easily prepared and preserved.

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ON THE REDUCTION OF SULPHURIC ACID BY COPPER, AS A FUNCTION OF THE TEMPERATURE.¹

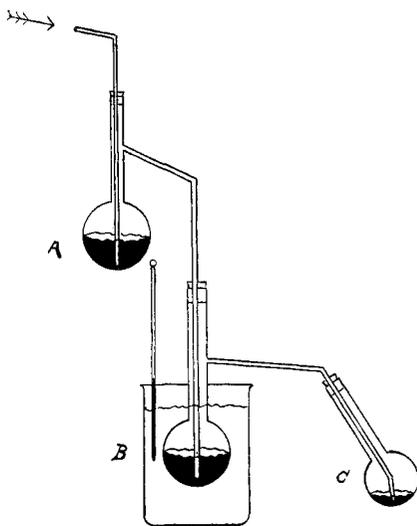
BY LAUNCELOT ANDREWS.

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

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

The method resorted to 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 carbon dioxide through it. The escaping gas was then tested (in flask *C*) by suitable reagents, to be described, for sulphuric and sulphurous acids respectively. Flask *A* contained concentrated sulphuric acid at the ordinary temperature (25° C.) to dry the gas, which was passed at the rate of about eighty bubbles per minute, except when otherwise men-



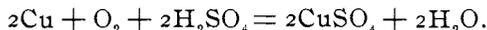
¹ Read before the Iowa Academy of Sciences, January 2, 1896.

tioned. The importance of securing absence of dust being recognized, the whole interior of the apparatus was washed with boiling concentrated sulphuric acid, then with water 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 *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, but 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 sulphur trioxide, that is, it begins to dissociate at a temperature lying between 60° and 70° C. and nearer to the latter.

Experiment II.—The apparatus was charged as before, with the addition of pure bright copper wire in *B* and with highly dilute iodide of starch in *C* instead of barium chloride. After passing air for several hours at the ordinary temperature, much of the copper had gone into solution and anhydrous copper sulphate had crystallized 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 carbon dioxide¹ 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° C. the solution in *C* was bleached.

In a similar experiment a solution of dilute sulphuric acid colored pale straw yellow with potassium bichromate was used as an indicator for sulphurous acid in *C*. In this case the change

¹ Freed from oxygen by bubbling through chromous acetate.

of color did not occur until the temperature had risen to 108°C ., the indicator being, as might be expected, less sensitive than the other.

Experiment IV.—This resembled III, except that a reagent for both sulphuric and sulphurous acid was used in *C*. This reagent was prepared by slightly acidifying a semi-normal 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 0.01 milligram of sulphurous acid.

When the temperature of the bath had reached 70°C . the solution in *C* was distinctly turbid with barium sulphate, but its color was unaltered. At 86° it began rather suddenly to bleach, and at 87° 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 or three bubbles per second.

The conclusions to be drawn from this investigation are :

First. That the dissociation¹ of sulphuric acid of 98.4 per cent. begins to be appreciable at a temperature somewhat below 70° , which may be estimated at 67°C .

Second. The reduction of sulphuric acid by copper does not begin below 86° , that is not until the acid contains free anhydride.

The assertion made by Baskerville² that sulphuric acid is reduced by copper at 0° 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 shown³ in consequence of the presence of air. I believe that a repetition of his experiments under conditions securing entire absence of oxygen can but lead him to a conclusion different from that to which he now adheres.

¹ The appearance of barium sulphate in *C* can not be accounted for by an assumed volatility of sulphuric acid as such, but only by its dissociation, because volatilized sulphuric acid would condense in the cold tube between *B* and *C*, since it has been shown that the acid was not appreciably volatile at the temperature of the latter. Hence only the anhydride could pass this cold tube and appear as sulphuric acid in *C*.

² This Journal, 17, 908.

³ Traube has shown the same thing for dilute sulphuric acid. *Ber. d. chem. Ges.*, 18, 1888.

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 of the copper or by Traube's theory, which is backed up by *almost* convincing evidence.¹

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

I hope to complete before long another series of experiments, now under way, which will form in a future communication a further contribution to the subject of the present paper.

THE OXIDATION OF SILVER.

BY CHARLES E. WAIT.

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IN a former paper² I had occasion to call attention to the large amount of silver present in a sample of bismuth litharge from a western smelting and refining company. The silver in this instance estimated in the metallic state was 2.94 per cent.

There was some doubt expressed as to the condition in which the silver existed, it being usually reported in the metallic state. Upon investigation it was found, as was shown in the paper referred to, that the silver did not exist wholly in the metallic state, but partly in another form, probably the oxide.

The conclusions reached at that time were based upon the following experiments:

1. A weighed sample of the litharge was boiled in acetic acid for about half an hour, the solution was filtered, and the filtrate gave no reaction for silver.

2. Same as above, but with continued boiling, the filtrate gave no reaction for silver.

3. A sample was placed in cold acetic acid, kept there for half an hour, then heated to boiling, the solution was filtered, the lead was precipitated, and in the filtrate silver was found to exist, corresponding to 19.25 per cent. of the silver in the litharge. Other determinations gave closely agreeing results, and

¹ Moritz Traube, *loc. cit.* and *Ber. d. chem. Ges.*, 18, 1877.

² *Trans. Am. Inst. Min. Eng.*, 15.