19. Analysis of Concentrated Sulfuric Acid and Fuming Sulfuric Acid by Thermometric Titration.

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There are many exothermic reactions, but that of water and fuming sulfuric acid is one of the best known among them. When fuming sulfuric acid was added to concentrated sulfuric acid in certain definite portions, the temperature of the solution rose as shown by A, B, and C in the figure; but after the entire water combined with fuming sulfuric acid, the temperature rose no more as shown by D, E and F. Therefore, the intersection of the lines ABC and DEF could be considered as the endpoint of the chemical reaction: \( \text{H}_2\text{O} + \text{SO}_3 = \text{H}_2\text{SO}_4 \). Such a thermometric titration as just described may be used to test the quality of chemicals and to control manufacturing processes as one of the methods of technical analysis. The apparatus consisted chiefly of a buret, and a large test tube placed in a Dewar's vessel and fitted with a stopper, through which were fitted a thermometer (1/10 or 1/20°C), a stirrer and the tip of a buret. A suitable quantity of the sample was poured into the test tube, which was then placed in the Dewar's vessel,

1) Strictly speaking the temperature somewhat rose or fell according to the degree of the concentration of fuming sulfuric acid and the temperature of the solution to be titrated.
and the temperature was read after the definite portions of the standard solution were added from the buret. However, it was difficult for the experiment if there was a great difference between the temperature of the sample and that of the room; therefore, the proper amount of fuming sulfuric acid was first poured into the tube and cooled to the room temperature, and then titrated as above.

1. **Determination of water content of concentrated sulfuric acid.**

As the standard solution commercial fuming sulfuric acid containing 10–25% of free sulfur trioxide was used and thermometrically standardized against pure water, or the water which was added to a known amount of concentrated sulfuric acid, or sulfuric acid, whose water content had been determined accurately previous to the standardization by acidimetry or the measurement of specific gravity. Such method of standardization seemed best suited for this analysis. The result of the standardization of about 25% fuming sulfuric acid showed that 1 g. of 80.09% sulfuric acid was equivalent to 1.818 ± 0.0007 (probable error) cc. of fuming sulfuric acid, and the result of the titration of concentrated sulfuric acid of 97.8%\(^1\)

with this fuming sulfuric acid showed that 1 g. of the sample was equivalent to 0.1964 ± 0.00006 cc. Therefore, the water content was 2.152%.

When compared with the indirect analysis of water in concentrated sulfuric acid by acidimetry, this thermometric titration is far more accurate as above shown and simple in the procedure of analysis and standardization. It is most suitable for the analysis of concentrated sulfuric acid of 90% or more.

2. **Analysis of fuming sulfuric acid.**

The sulfuric anhydride in fuming sulfuric acid was determined thermometrically in the presence of sulfur dioxide using fuming sulfuric acid as the standard solution. Fuming sulfuric acid to be analysed was taken in a tube, and 80.09% sulfuric acid was added into it in a little greater quantity than just enough to decompose the fuming sulfuric acid, and then the water left uncombined was titrated with 25% fuming sulfuric acid which had been standardized against 80.09% sulfuric acid. Let \(a\) be the weight of the sample taken; \(b\), the weight of 80.09% sulfuric acid; \(c\), cc of the standard solution of fuming sulfuric acid equivalent to 1 g. of water; \(d\), cc of the standard solution added from the buret for the back titration;

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\(^1\) This value was determined by acidimetry.
x, the percentage of free sulfur trioxide in the sample; then, x was computed from \(0.1991 \times b - \frac{d}{c} = \frac{18.02}{80.08} \times a \times x \times 10^{-2}\). The result of the analysis showed that the free sulfur trioxide in the so-called 65% commercial fuming sulfuric acid was 64.86, 64.79, 64.81, 64.86, or 64.78%; and that in the 25% fuming sulfuric acid was 28.02, 28.01, 27.98, or 28.02%.

When compared with the analytical methods of fuming sulfuric acid known up to date, this thermometric titration is better and simpler in its procedure and standardization, especially in the case of analysis of highly concentrated acids; and, perhaps, most accurate of all methods, the percentage error of a single determination being below 0.05 per cent.