NOTES ON THE SPECIFIC GRAVITIES OF LIQUID AND SOLID SULPHURIC ACID

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ABSTRACT.

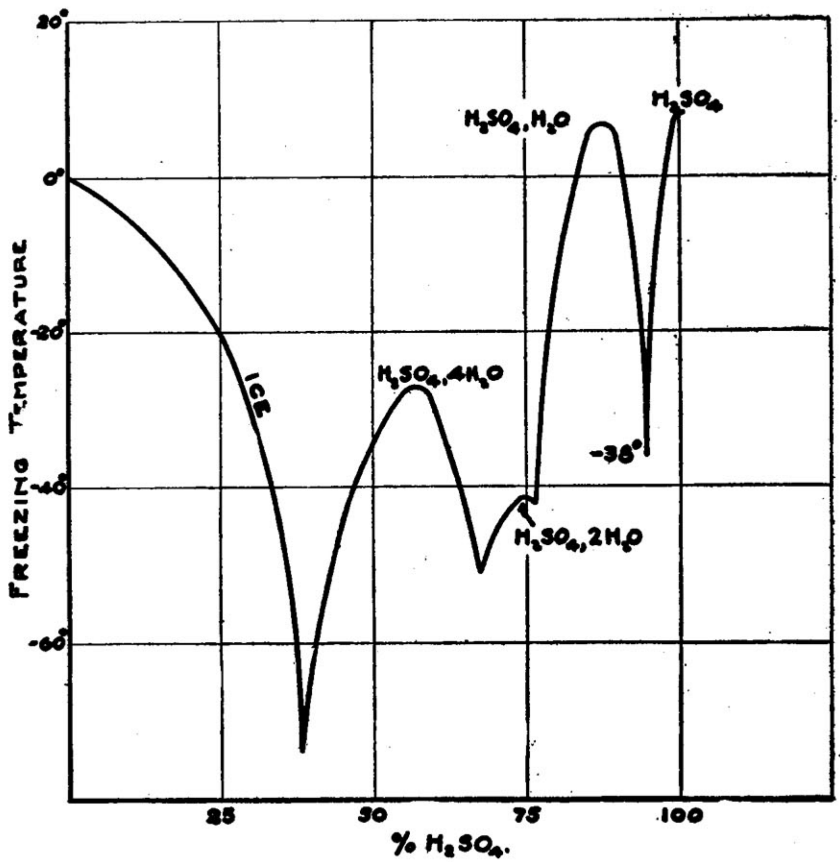
The specific gravities of sulphuric acid of approximately 60° and 66°Bé in both the liquid and solid states are given together with some observations on the supercooled acids.

Some years ago I was asked for an explanation of the destruction of a number of carboys of sulphuric acid. These were stored in the yard of an industrial plant, a custom followed for many years without loss, until the day before, when about fifteen were found broken, and the acid entirely lost. The temperature for a number of nights had fallen almost to zero, while the bright sun at mid-day warmed opaque objects to quite a high temperature.

My first impression was that the sulphuric acid expanded on freezing, and that the destruction of the carboys was due to this. A simple experiment showed that sulphuric acid between 60° and 66° Bé—the acid supplied varied in strength—behaved as a normal substance, being denser in the solid than in the liquid state. In attempting recently to make some more exact determinations of the density of the solid acid a number of the bulbs filled with the acid were broken. I shall give here some of the results obtained and a probable explanation for the failure of the carboys.

The specific gravity of the liquid acid was measured in the ordinary way in calibrated bulbs with graduated stems of capillary tubing. The bulb, containing a weighed amount of the acid, was kept in an appropriate constant temperature bath until its volume was constant. Sulphuric acid of any composition between 60° and 66° Bé could be kept in solid carbon dioxide almost indefinitely without crystallization taking place. When a crystal formed, or was introduced at this temperature, the growth of the solid was extremely slow. At a few degrees below the true freezing-point, these liquids froze rapidly, particularly on stirring. We have here a good example of a supercooled liquid.

The determination of the density of the solid is not easy, and the results can be looked on only as approximations. The sulphuric acid was frozen in the bulb with a calibrated stem, partially remelted, and this was repeated again and again, in order to fill, if possible, all interstices in the solid. (At times, the partly frozen mass was centrifuged). The bulb, completely filled with the solid acid, was placed in the constant temperature bath, and the total volume determined while the capillary



contained only liquid. From the specific gravity of the liquid which was known, that of the solid was calculated.

The results for approximately 60° and 66° Bé acids are given in the table.

60° Bé	Temp.	Sp. Gr.	66° Bé	Temp.	Sp. Gr.
Liquid	+15°	1.695		+20°	1.838
	—40°	1.756		—78.5°	1.951
	—78.5°	1.801			
Solid	—43°	1.797		—78.5°	2.040
	—60°	1.811			
	—78.5°	1.838			

As mentioned before, a number of bulbs were broken during the experiments, but always with rising temperatures. Apparently the solid sulphuric acid, in certain circumstances, adheres to the upper part of the bulb, and so prevents the free expansion of the liquid. This, I believe, furnishes a satisfactory explanation of the fracture of the carboys.

The diagram shows the freezing-points of sulphuric acid at various concentrations as given in the tables. In the transportation of acid in tank cars in winter, it might be possible to adjust the concentration at times, so that freezing would not take place thus avoiding the disagreeable task of melting the acid with a steam jet.