

ART. II. — ON THE RELATIVE BULK OF CERTAIN AQUEOUS SOLUTIONS AND THEIR CONSTITUENT WATER.—  
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THE following experiments were made with the object of determining whether or not weak solutions of Sodium Phosphate and Carbonate have volumes which are less than the volumes at the same temperature of the water which they contain.

Professor Ewing and I had found that sufficiently weak solutions of sulphate of copper contain amounts of water whose volumes if free would be greater than those of the solutions themselves; and that anhydrous copper sulphate, added in small quantities to water, produces solutions of smaller bulk than the original water. It seemed desirable therefore to extend the investigation to other hydrated salts.

The apparatus employed consisted of dilatometers, which were large glass bottles (commonly called Winchester quarts), with glass tubes fitted in their necks. The bottles had capacities of about 2,600 c.c. The glass tubes were about 25 cm. in length and 0.4 sq. cm. in section, and were chosen so as to be as uniform in bore as possible. They were fitted to the bottles by means of India-rubber stoppers, and fitted so tightly that there could be no danger of any relative displacement of tube and bottle. The rubber stoppers were held fast to the bottle by wires. Their inner ends were hollowed conically, and the glass tubes started from the summits of the conical hollows, so that air bubbles could easily be made to pass up the tubes. At their upper ends the tubes widened into funnels. Fine scratches on the tubes served as zero marks. The bottles stood in a large zinc bath up to their necks in water. The dilatometers were calibrated by

<sup>1</sup> Trans. Roy. Soc. Edin., vol. xxvii. (1873) p. 51; Reports Brit. Asso. (1877); Trans. Roy. Soc. Canada, vol. ii. (1884) sec. iii., p. 69.

being filled with distilled water of known temperature, from measuring vessels whose volumes were known. The one used in calibrating the tubes was so divided that changes in the volume of the water it contained could be read to 0.05 c.c. The water, with which the bottles were thus filled, had been freed from air under the receiver of an air-pump.

To test the tightness of the stoppers, the dilatometers were filled, until the upper surfaces of the water were near the tops of the tubes. The stoppers were thus subjected to as great pressures as they would be during the experiments. After the bottles had taken the temperature of the bath, I observed the variation of the height of the water in the tubes from time to time, until I had satisfied myself that there was no leak,—a return to a formerly observed height in one bottle being accompanied in all cases by a similar return in the others.

I next satisfied myself that differences of temperature between the bottles, greater than any which could arise during the experiments through the dissolving of salt in some bottles and not in others, would vanish in less than the time that was to intervene between successive measurements.

As the dilatometers could not be kept at constant temperature, and as any change of volume of their contents must therefore be partially due to change of temperature, it was necessary to know the relative apparent thermal expansion of their contents. For this purpose, both at the outset when all the bottles contained water, and at intervals during the series of experiments when some of them contained solutions, the temperature of the bath was varied, and the heights of the water or solutions in the different tubes were observed when the bottles had assumed the temperature of the bath. These results were tabulated for purposes of correction.

The solutions, whose volumes were measured, were formed by the addition of known masses of anhydrous salt to the water in the bottles. The salt was simply dropped little by little down the tubes of the dilatometers. Occasionally the salt was found to cake at the surface of the liquid. In that case various expedients were adopted to hasten the solution; but the greatest

care was taken to prevent the loss, either of any of the salt which had been weighed out for solution, or of any of the liquid in the bottles. When the desired amount of salt had been added to a bottle, the upper end of the tube was closed with a small cork to prevent evaporation, and the bottle was put in the bath. After an interval of about twenty-two hours the bottle was taken out, and, if the salt was found to be dissolved, was first well corked, and then rolled, until its contents had been thoroughly mixed. It was then replaced in the bath and left for another hour, when the height of the free surface of the liquid was observed. Not possessing a cathetometer, I required, for measuring differences of level, to trust to a steel scale placed in contact with the tube. Care was of course taken to avoid parallactic errors as much as possible.

To one of the bottles no salt was added; and it was kept carefully corked up, so that the quantity of water it contained might be constant. The variation of the height of the water in the tube of this bottle was due, of course, to change of temperature alone. This variation being observed, and the relative apparent thermal expansions of the liquids in the four bottles being known from the subsidiary experiments referred to above, the variations due to changes of temperature, of the heights of the solutions in the tubes of their respective bottles could be determined and eliminated. The variations of temperature were in all cases slight, the bath being large and its daily thermal history being very constant.

The salts used, the acid phosphate of Sodium ( $\text{H}_2 \text{Na PO}_4 + 12 \text{H}_2 \text{O}$ ) and the basic carbonate of Sodium ( $\text{Na}_2 \text{CO}_3 + 10 \text{H}_2 \text{O}$ ) were bought as pure, repurified by crystallization, and dehydrated by careful heating to the necessary temperature.

In all cases, after the solutions had stood awhile, a slight fluffy appearance presented itself in the bottles. The mass of the precipitated solid was, however, very small—so small that it was hardly possible to weigh it. Hence I considered that its effect on the result might be neglected. It was probably due to the presence of some impurity in the water.

In both cases I found weak solutions of these salts to have

smaller volumes than their constituent water would in the free state possess. In the case of the phosphate, this is true of all solutions containing less than about 0.016 per cent. of the anhydrous salt, the difference of volume being greatest in solutions containing about 0.011 per cent. A solution of this strength, containing 1000 cubic inches of water, has a volume of 999.87 cubic inches. In the case of the carbonate I found the greatest difference of volume to occur with a solution containing about 0.026 per cent. of anhydrous salt, a solution of this strength which contained 1000 cubic inches of water having a volume of 998.27 cubic inches.