

ART. LI.—*The relations of the Volumes of Solutions of Hydrated Salts to their Water of Composition*; by RICHMOND J. SOUTHWORTH, M.D.

THE object of the experiments, the result of which is stated in the accompanying table, was to test this

*Theorem: If a hydrated salt be dissolved in a given volume of water, the volume of the solution will exceed the original volume of the water by a bulk equal to the bulk of saline water contained in the salt dissolved.*

The expression *saline water* is used here to signify all the molecules of water contained in the salts, whether they exist in combination as bases, or as water of crystallization. First, the weight in grams of the salt used that contained one cubic centimeter of water in its composition was determined by dividing the atomic weight of the salt by the atomic weight of its saline water, both weights being expressed in grams, the quotient gave the weight, having one cubic centimeter of saline water. As an example: Ferrous sulphate ( $\text{FeSO}_4, 7\text{H}_2\text{O}$ ) has an atomic weight of 278. Its 7 molecules of saline water have an atomic weight of 126.  $\frac{278}{126}$  grams = 2.206 the weight of this salt having one cubic centimeter of water in its composition.

Second: The quantity of salt determined by this method to contain one cubic centimeter of saline water was weighed to the nearest centigram, and then dissolved in 90 c.c. of water in a graduated tube of 100 c.c. capacity divided in one-half cubic centimeters. For instance, 2.20 grams of  $\text{FeSO}_4, 7\text{H}_2\text{O}$ , were dissolved in 90 c.c. of water at the temperature of  $15.5^\circ$  Centigrade when the volume of the solution equalled 91 c.c.: 2.20 grams more of the salt were added to this solution, and the volume rose to 92 c.c. This process was continued till 22.06 grams of the salt, containing 10 c.c.  $\text{H}_2\text{O}$ , were dissolved in 90 c.c. of water, when the volume of the solution reached 100

c.c. In each of the steps, and in the final result, this experiment agreed with the theorem. This method was pursued where the first experiment with a salt showed a close agreement with the theorem. In those cases where there was a disagreement between the calculated volume and the observed volume of the solution, the weight of salt required to raise the volume of the solution one cubic centimeter was determined by direct experiment. For instance, barium chloride, with the formula  $(\text{BaCl}_2 \cdot 2\text{H}_2\text{O})$  by calculation contained one cubic centimeter of  $\text{H}_2\text{O}$  in 6.777 grams, but the quantity required to raise the volume of the solution one cubic centimeter was 3.89 grams. If the specimen of barium chloride used contained  $4\text{H}_2\text{O}$ , the experiment would give a result agreeing with the terms of the theorem.

Salt used.	By calculation.	By experiment.
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	1.588	1.59
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	1.788	1.63
$\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$	4.083	3.25
$\text{Na}_2\text{O}_2\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$	2.122	2.12
$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	1.591	1.59
$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	6.777	3.89
$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	2.468	2.47
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	1.954	1.95
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	2.277	2.28
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	2.228	2.23
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	2.206	2.2
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	2.771	2.77
$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	2.058	2.06
$\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	2.196	2.2
$\text{AlNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	2.099	2.1
$\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	2.31	2.31

The first column of the table gives the formulæ of the salts according to the last American edition of Fownes's Chemistry. The second column gives the weight in grams that contains one cubic centimeter of saline water, according to the formula. The third column gives the weight in grams found by experiment to increase the volume of the solution one cubic centimeter. An examination of the table will show a close agreement between the results of calculation and experimentation, with the exception of barium chloride, which has been referred to, and the acid sodium sulphate. The disagreement between the calculation and observation in this instance may possibly be explained by the salt decomposing in the act of dissolving, separating into sodium sulphate, which is dissolved, and hydrogen sulphate which unites with the water. This would agree with the strong acid reaction of the solution.

So far as the salts used in these experiments are concerned, the theorem stands the test of experiment, and is demonstrated to be true. In explanation of the changes that occur when a hydrated salt is dissolved in pure water, it may be assumed that the salt is decomposed, separating into an anhydrous portion and saline water, the former going into solution and the latter uniting with the solvent water, increasing its volume.

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