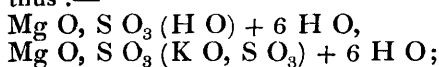


XIV. *On the Constitution of the Sulphates as illustrated by late Thermometrical Researches.* By THOMAS GRAHAM, Esq., F.R.S., &c.

Read January 18, 1842.

PROF. Hess and Dr. Andrews both apply the results of their late inquiries respecting the heat evolved in combination* to test the accuracy of a view of the constitution of double and acid salts which was published by myself, and arrive, it is remarkable, at opposite conclusions.

The view in question, I may first state, taking the example of double and acid sulphates. Crystallized sulphate of magnesia, and the double sulphate of magnesia and potash, I have represented thus :—



considering the latter salt to be derived from the former, by the substitution of sulphate of potash for that single atom of water, which is found to be much more strongly attached to the sulphate of magnesia than the other six. This atom of water, which is not basic water, was formerly named *saline* water, to indicate that it is replaceable by a salt; its presence being considered a provision in sulphate of magnesia for the formation of double salts. The water and sulphate of potash are therefore looked upon as equivalent in the construction of the two salts; and the substitution of the salt for the water might therefore be reasonably expected to occur without the evolution of heat.

* Phil. Mag., January 1842.

In accordance with that statement, Dr. Andrews finds that no heat is evolved on mixing solutions of sulphates of magnesia and potash, nor in the formation of any other double salt. On repeating the experiment I found also no heat nor change of temperature on mixing the solutions, although a change of $\frac{1}{20}$ th of a degree Fahr. would have been distinctly indicated by my thermometer.

Possibly, however, the double salt may not immediately be formed, and hence no change of temperature at the moment of mixing the two solutions, nor for some time afterwards. To meet this objection, solutions of sulphate of magnesia and of sulphate of ammonia (the last, from its greater solubility, being preferred to sulphate of potash) were made of such a strength that they might be mixed without the precipitation of the double salt immediately occurring, but strong enough to allow a large quantity of the double salt to fall upon stirring the liquid strongly. The solutions were 1546·88 grains of cr. sulphate of magnesia dissolved in so much water as to form 8000 water grain measures, and 613·5 grains oil of vitriol, neutralized with ammonia and made up to 4000 water grain measures. On mixing one ounce measure of the first with half an ounce measure of the second, both exactly at 50°, not the smallest change of temperature could be observed; but as soon as the double salt began to deposit, the temperature rose, and on stirring strongly much salt was deposited, and the temperature rose 5·40° Fahr. On re-dissolving this salt, however, by substituting for the mother liquor an equal bulk of water, the temperature instantly fell 5·85°. Hence the heat which first appeared was produced by the solidification of the double salt, and disappears upon its liquefaction. There is no heat referable to combination of the two salts. The cold on dissolving was always somewhat greater than the heat on precipitating the double salt, in repetitions of this experiment, chiefly, I believe, from the slowness of the precipitation, which requires a minute or two, so that a portion of the heat is lost from contact with the atmosphere, and the whole not observed, while the subsequent solution of the salt being almost instantaneous, the whole fall of temperature is observed. The same experiment was made with a solution of sulphate of zinc, of the same strength as the sulphate of magnesia, and with similar results, only that the fall of temperature, on solution, was somewhat less than that on solidification, namely, as 9°·22 to 9°·67, difference 0°·45 Fahr. This was principally owing to the time required in re-dissolving this double salt being greater than that occupied in precipitating it, three applications of

water being required to re-dissolve the double salt completely, owing to its sparing solubility.

M. Hess's objection is made to the analogous constitution which I have assigned to the bisulphate of potash :—

Sulphuric acid of specific gravity 1·78, $\text{H O, S O}_3 (\text{H O})$.

Bisulphate of potash $\text{H O, S O}_3 (\text{K O, S O}_3)$.

He maintains that heat is evolved in the formation of a bisulphate, and therefore that the combination is not effected by the equivalent substitution supposed. He mixed sulphate of potash with $\text{H O, S O}_3 + \text{H O}$, and found heat evolved, but allows that the result here is fallacious, a portion only of the sulphuric acid being converted into bisulphate, while the other portion is diluted by the displaced water of the first portion, and thus heat evolved.

On performing the direct experiment, which M. Hess appears to have neglected, using a saturated solution of sulphate of ammonia, and sulphuric acid of specific gravity 1·256, I obtained, on mixing, $5\cdot4^\circ$ of cold instead of any heat. But on diluting the sulphate of ammonia with a volume of water equal to that of the dilute acid, a fall of $1\cdot12^\circ$ occurred. Deducting this from the former, there remains a fall of $3\cdot88^\circ$ due to the combination of the two salts, sulphate of water with sulphate of ammonia. But this may be explained. The bisulphate of ammonia formed is an anhydrous salt, unlike the double sulphate of magnesia and ammonia, which carries along with it all the water of crystallization of the sulphate of magnesia. But the sulphate of water itself, as it exists in diluted sulphuric acid, is a largely hydrated salt, like sulphate of magnesia. The water of the former, on being set free in the last experiment, absorbs heat, because heat was evolved originally in the combining of this water with the sulphuric acid.

Although certain small corrections on these experiments for changes in capacity for heat of the liquids have been neglected, yet they are sufficient to demonstrate that no heat is evolved in the formation of double sulphates, and also, as appears by the last experiment, that these compounds are formed at once on mixing the solutions of their constituent salts, whether precipitation occurs or not. Sulphate of potash and water are therefore equivalent in the constitution of such salts, or *equi-calorous*, if a term may be coined to express this relation.