X.—*The Heat of Hydration of Salts. Cadmium Chloride.*

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DURING the recent discussion on the nature of solution at the Birmingham meeting of the British Association, Dr. Nicol drew attention to and laid considerable weight on the supposed fact that the heat of hydration* of cadmium chloride was a negative quantity (*Chem. News*, 54, 191). His line of argument would appear to be as follows: The heat developed on the hydration of a salt does not give any measure of the affinity of the salt for solid water, for other (unknown) physical changes must occur at the same time, as is proved by the heat of hydration bearing no relation to the degree of hydration, and by the existence of an instance, cadmium chloride, in which the heat of hydration is actually a negative quantity, all spontaneous chemical changes being exothermic. *Quâ* argument this appears to me to be very insufficient. What is observed in the hydration of a salt is repeated in every instance of chemical combination. Thus, in the chlorination of various metals, the heat developed *per* atom of chlorine bears no relation to the number of atoms which are assimilated; and if we are permitted to assume various unknown physical changes as being to a great extent the cause of the heat evolved in the combination of two substances in the same state, we must at once reject all thermochemical evidences. The statement that all spontaneous chemical changes are exothermic is itself robbed of whatever truth it may contain, for we may in every case, as here, doubt the change being a purely chemical one.

My attention had previously been attracted to the case of cadmium chloride, not so much on account of its heat of hydration being negative, but that it was absolutely the only known instance of an inorganic salt where such a fact occurred. As the heat of dissolution of the salts had been determined only once (by Thomsen, *Thermo-chem.*, 3, 201), it seemed not altogether improbable that some mistake had arisen, and I therefore determined to repeat the work.

Two samples of the anhydrous salt were prepared, one at 200°, the other being fused. The results which are given in the accompanying table† (see p. 76) can only be regarded as approximations; for, on the

* By "heat of hydration," I mean throughout the number obtained after due allowance has been made for the heat of fusion of the water present in the hydrated salt.

† For the calculation of results and other details, see *Trans.*, 1886, 266.

one hand, it was found impossible to dehydrate the salt completely without fusion, while, on the other, fusion was impossible without a certain amount of decomposition (the specimen No. 2 contained 0.5 per cent. of oxide). The numbers, however, are sufficiently concordant to show that the fused and unfused salts give practically the same results (3382 and 3211 cal. respectively), and that these are identical with that obtained by Thomsen (3011 cal. at about 18°).

Heat of Dissolution of the Chlorides of Cadmium in 400 H₂O.

Substance.	Weight taken.	Heat equivalent of solution, &c.	Initial temp.	Rise of temp.	Observed heat of dissolution.
CdCl ₂ .					
1. Prep. at 200° C.	15.168 grms.	610.04 grms.	18.14° C.	0.4609° C.	3382 cal.
2. Fused	15.125 „	610.04 „	18.135° „	0.4364 „	3211 „
CdCl ₂ .H ₂ O.					
3.	16.717 „	611.54 „	18.135 „	0.0853 „	625 „
CdCl ₂ .2H ₂ O.				Fall of temp.	
4.	18.200 „	613.22 „	18.00 „	0.3104 „	-2284 „

The hydrated salt (No. 3), on dissolution at the same temperature, gave 625 cal., a number evidently identical with that obtained by Thomsen—760—but on analysis it was found to consist of a monohydrate, instead of a dihydrate as Thomsen states, containing 9.617 per cent. water; theory, 9.120 per cent.

This monohydrate was uniformly obtained whenever a solution of the salt was evaporated at a high temperature; when, however, a cold solution was evaporated, crystals, not easily distinguishable from the monohydrate, were obtained, but consisting of the dihydrate, containing 17.035 per cent. water, the theoretical number being 16.450 per cent. This dihydrate, on dissolution, absorbed 2284 cal.

It is evident, therefore, that some error must have occurred in Thomsen's statement; he certainly used the monohydrate in the calorimetric determination, and, unless his entry that it was found on analysis to contain 2.01 H₂O be a mere *lapsus calami*, it is probable that the analysis was performed on a different specimen, prepared, as he imagined, under identical conditions, but in reality at a lower temperature.

According to the numbers here given, the heat of hydration of cadmium chloride is by no means a negative quantity [CdCl₂ + H₂O

(solid)* being 1092 cal., and $[\text{CdCl}_2 + 2\text{H}_2\text{O (solid)}]$ 2421 cal. or 1210×2 , numbers which are considerably larger than in the case of sodium carbonate (588 cal. per H_2O), strontium nitrate (421 cal.), and sodium sulphate (320 cal.).

Amongst organic substances, there is one salt in which the heat of hydration would appear to be negative, sodium benzenesulphonate, — 250 cal. per H_2O , besides the case of racemic acid, in which it is exactly *nil*. This latter instance has been well established, and, in my opinion, tends to show that the so-called hydrated acid does not contain water of crystallisation at all, but possesses a constitution different from that of the anhydrous acid; a similar explanation may hold good with the sodium benzenesulphonate, but, as this instance rests at present on one determination only (Berthelot's), it should in the first place be more fully investigated.