XXII.—*On the Dehydration of Hydrates by the Time Method.*

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PART I. *Iron and Aluminium Hydrates.*

THE hydrates of the metals have, as a rule, been accepted as definite substances, and have been supposed to bear analogy to the chlorides, bromides, nitrates, &c., in their formulæ; for example, it is customary to represent ferric hydrate by the formula $\text{Fe}(\text{OH})_3$, analogous to ferric chloride, FeCl_3 , or by the double formula, $\text{Fe}_2(\text{OH})_6$, analogous to Fe_2Cl_6 . But statements about the hydrates of iron, aluminium, chromium, and many other metals, vary so much, that it appeared desirable to revise the subject, and to ascertain under what circumstances definite hydrates, if they do indeed exist, can exist.

I am indebted to my friend, Mr. Hannay, for the principle of the method employed in this investigation; viz., to determine the loss of water of the hydrates when dried at a constant temperature, at regular intervals of time. In the case of crystalline bodies containing

water, as shown by Mr. Hannay, in the preceding paper, the water is given off at a certain rate till a certain number of molecules have been expelled; the rate then changes and usually becomes slower, keeping pretty constant till a lower stage of hydration has been reached; the water is then evolved at a different rate, and this goes on till all the water of crystallisation in the salt has gone.

The following hydrates of alumina have been described:—1st. The trihydrate, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, obtained as a gelatinous precipitate by adding ammonia to a concentrated solution of a salt of aluminium, and drying (in air?); 2nd. The dihydrate, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, prepared by heating aluminium acetate to 100° for some days, and drying the resulting precipitate at 100° ; 3rd. The monohydrate, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, found native as diaspore. If these hydrates are definite chemical substances, it is to be expected that they should exhibit different vapour tensions, and that in drying by the time method, the rate at which the water is given off should be different for each hydrate; if, on the other hand, they are not definite, the water should be expelled at a constantly decreasing rate, without showing any sudden change when the substance passes from one state of hydration to another.

The aluminium hydrate was precipitated from a boiling solution of the chloride with ammonia; the chloride had been obtained by dissolving in hydrochloric acid alumina precipitated from alum with ammonia, again precipitating as hydrate, and again dissolving. It was then washed free by decantation, not only from hydrochloric acid, but until it gave a hardly perceptible coloration with Nessler's reagent; and it was dried by exposure to air for a number of weeks. It formed a hard, horny substance, which, although it could be scratched with a knife, yet had to be reduced to powder in an agate mortar. Its composition was found to be—

$$\text{Al}_2\text{O}_3 = 54.08 \text{ per cent.}$$

$$\text{H}_2\text{O} = 45.92 \quad ,,$$

The formula, $\text{Al}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ requires 53.33 per cent. Al_2O_3 , and 46.67 per cent. of water.

The method of drying the hydrate was as follows:—A watch-glass filled with the powdered hydrate was placed in a bath, heated to a constant temperature. After a certain time had elapsed (depending on the expected loss of water), the watch-glass was removed and placed over sulphuric acid for ten minutes to cool; it was then weighed, and again placed in the bath. When the loss became so small as to be unweighable, the temperature was raised, and a new set of experiments begun.

In the accompanying graphic representation, the ordinates of the Curves I, II, III, IV, and V represent minutes; the abscissæ, the

amount of water per cent. It will be seen, by reference to the diagram, that Curve No. I splits rather above 40. This represents the fact that the hydrate, after drying for 50 minutes, contained 38·7 per cent. of water; after standing in air over night, at a temperature of 14°, it had gained 2 per cent. of water, which were given off next day at 71°, at a different rate from that at which it had been evolved originally. From this it appears probable that the water absorbed was combined less closely with the alumina than that at first given off. The rate of evolution of water at 71° differs very slightly from that at 100° (II), and it is noticeable that no break of continuity occurs. Now the hydrates, $\text{Al}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, contain respectively 41·18 per cent. and 34·43 per cent. of water; and were the vapour-tensions of these hydrates different from each other, and different from those of $\text{Al}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, and of alumina at a lower degree of hydration than $3\text{H}_2\text{O}$, it is probable that a break of continuity would occur, and that the curve, instead of approximating to a straight line, would alter its direction at two distinct points. $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ contains 25·93 per cent. of water, and $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, 14·90 per cent.; the former is passed at a temperature of 145°, without any sudden change of rate, and the latter is nearly, but not quite, reached at a temperature of 300°.

On ignition of the hydrated alumina containing 14·95 per cent. of water, the powder is moved about in a curious manner by the escaping steam; the escape of water appeared to go on of its own accord after it had been induced by application of heat, for on removing the flame, the motion of the powder did not cease. It was evidently undergoing the change from the soluble to the insoluble modification of alumina, which is possibly accompanied by evolution of heat.

Curve No. VI represents the rate at which alumina loses water over oil of vitriol. It is the result of only three measurements, each ten spaces representing one day of 24 hours. The rate, as was to be expected, is slower than at 71°, but the amount of dehydration is as great as was reached at 100°. On weighing again, after four days, it was found to have gained water, owing probably to a slight change of temperature.

The rate of loss of water of ferric hydrate is graphically represented in Curves VII, VIII, IX, X, and XI. The percentages of water required by theory for the different hydrates are these:— $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ requires 31·03 per cent. H_2O ; $\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, 23·46 per cent.; and $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, 10·11 per cent. The hydrate dried in air had, on one occasion, nearly the percentage of water required by the formula $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$; but another specimen, perfectly dry to all appearance, and so hard, that it had to be reduced to powder in an agate mortar, contained 34·00 per cent. of water. It is again evident that no sudden

break of continuity occurs, except at 100° ; from several experiments it resulted that the hydrate of iron, precipitated either from a cold or from a boiling solution, after being dried at 100° until no more water was evolved, had approximately the formula $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$; and this was the case, whether it was dried gradually at 50° and 75° before being heated to 100° , or whether it was placed in the water-bath in a moist condition. One of two conclusions is to be inferred from this fact; either that there exists a definite hydrate, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, or that the vapour-tension of water at 100° is coincidentally that of the combination of ferric oxide with water at the same temperature. If a coincidence, it is a curious one.

The dotted line in Curve No. IX represents the probable course of a curve showing the loss of water by ferric hydrate at 100° . The first weighing was made after three hours' exposure to 100° .

A dotted line will also be noticed in Curve No. X. The iron hydrate, after standing over-night over oil of vitriol, absorbed nearly 1.75 per cent., which it gave off after 20 minutes' exposure to 150° much more rapidly than it had done previously. This would again point to the conclusion that the water absorbed was not in such close combination with the ferric oxide as it had previously been.

The conclusions to be drawn from these results are as follows:—If there are only four or five hydrates of iron or aluminium, their vapour-tensions do not differ much from each other (with exception of that of $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$); the probability is, however, either that hydrates, such as $\text{Al}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, &c., have no existence, or that a very large number of hydrates of aluminium and iron exist, the vapour-tensions of which are very slightly different from each other, the smallest rise or fall of temperature being sufficient to convert a higher into a lower hydrate, or *vice versa*. It must always be understood that these conclusions apply only to the amorphous hydrates of the above-mentioned metals.

I have also made experiments on the hydrates of copper and lead with the view of ascertaining their true composition. Copper hydrate prepared by precipitating a solution of the chloride with warm baryta-water, washing the precipitate free from barium chloride, and drying in air, has the formula $\text{CuO} \cdot \text{H}_2\text{O}$.

Water found.....	20.88 per cent.
„ calculated.....	19.48 „

It loses very little water and preserves its colour at 120° , the amount of water at that temperature being 20.30 per cent. At 150° it begins to blacken and is slowly converted into the black oxide. This agrees with the results of Proust's experiments.

Lead hydrate, prepared from the nitrate by precipitation with excess

of baryta-water (used because of the difficulty of washing such hydrates free from potash or soda) and washed until free from barium nitrate, contained when dried in air 4.00 per cent. of water, agreeing thus with the formula $2\text{PbO} \cdot \text{H}_2\text{O}$, which requires 3.88 per cent. Over sulphuric acid for some weeks it lost water, but still contained 2.69 per cent., equivalent to $3\text{PbO} \cdot \text{H}_2\text{O}$, which demands 2.71 per cent. Both of these hydrates have been prepared: $3\text{PbO} \cdot \text{H}_2\text{O}$ by Tünnermann, from a cold solution of lead acetate and ammonia; by Payen, from a boiling solution of the same salt; and $2\text{PbO} \cdot \text{H}_2\text{O}$ by Schaffner, from lead acetate and potassium hydrate.

I propose to extend these researches to other hydrates, the results of which I hope to have the honour of laying before the Society.