XV.—*The Hydrates and the Solubility of Barium Acetate.*

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BARIUM acetate is well known to exist in three modifications, two of which are hydrated and one anhydrous. Thus it is stated in Gmelin's *Handbook* that when left to evaporate spontaneously in summer, the concentrated aqueous solution deposits crystals containing one molecule of water, whilst a less concentrated solution cooled to 0° yields

crystals containing three molecules of water. At 100°, the anhydrous salt is obtained.

The older data concerning the solubility of barium acetate are somewhat discrepant. It is stated in Kolbe's *Lehrbuch*, on the authority of Liebig, that the substance is more soluble in cold water than in hot. Bucholz (quoted in Storer's *Dictionary of Solubilities*) states, on the other hand, that the crystals (monohydrate ?) dissolve in 2.25 parts of water at the ordinary temperature and in 1.1 parts at the boiling point. Storer also quotes from Berzelius's *Lehrbuch* that the saturated cold solution contains 36 per cent., and the saturated boiling solution 50 per cent.

Tilden and Shenstone determined the solubility of barium acetate at temperatures ranging from 20° to 180° (*Phil. Trans.*, 1884, 175, 23). The curve by means of which they express their results shows a solubility of 48 parts of anhydrous salt in 100 parts of water at 20°, rising rapidly to 79 parts in 100 at 60°, thereafter to continue constant up to 100°. Since, however, Tilden and Shenstone were more immediately concerned with the solubility of the salt above 100°, they only performed three determinations below that temperature, so that the form which they give to their curve in the region below 100° cannot be regarded as conclusive.

Krasnicki (*Monatsh.*, 1887, 8, 601) determined the solubility of barium acetate monohydrate at temperatures between 0° and 80°, and found that his results could be expressed by the formula

$$S = 58.47 + 0.65067(t - 0.8) - 0.005431(t - 0.8)^2,$$

in which t is the temperature in centigrade degrees and S the solubility in parts of anhydrous salt dissolved by 100 parts of water. It appeared to us rather remarkable that a substance which was known to exist in two hydrated forms at low temperatures should give a single continuous solubility curve throughout such an extensive range.

From the behaviour of the hydrates detailed in Gmelin's *Handbook* one might expect to deal, between 0° and 100°, with three distinct solubility curves, for the trihydrate, monohydrate, and anhydrous salt respectively, which should cut in two transition points, and the chief object of this investigation was to ascertain if this were the case, and to determine as exactly as possible the transition temperatures for the conversion of trihydrate into monohydrate, and of monohydrate into anhydrous salt.

The barium acetate which we employed in the investigation was always recrystallised by ourselves. When the hot saturated solution was cooled to the laboratory temperature, the trihydrate separated out in needle-shaped crystals. This substance could not be kept in

the dry state, as it speedily effloresced and was partially converted into the monohydrate. The monohydrate which we employed was generally prepared from the trihydrate, this, after two days in an exhausted desiccator, lost two-thirds of its water and was completely converted into monohydrate. Under ordinary laboratory conditions, the monohydrate could be kept indefinitely without undergoing alteration. The anhydrous salt was prepared by heating either of the hydrates in a steam oven for several hours; usually two days were allowed in order to secure complete dehydration.

For the purpose of obtaining an approximate idea of the position of the inversion temperatures, a van't Hoff dilatometer was charged with the trihydrate and toluene. When placed in a thermostat at 20° , the reading of the toluene in the capillary remained constant for four hours, thus indicating no transformation at this temperature. At 35° , the toluene rose rapidly during the first hour and slowly during the next two hours, thereafter remaining constant for 20 hours. This behaviour indicated that between 20° and 35° the trihydrate undergoes transformation into a less hydrated form, the transformation being accompanied by an increase of volume. On heating now at 40° , no change of volume was observed during 3.5 hours, thus indicating no further transformation. At 45° , however, a slow diminution in volume was perceptible, lasting more than 20 hours. This second transformation, thus indicated between 35° and 45° , is accompanied by a diminution instead of an increase of volume. At 55° , no further volume change was observed.

In order to ascertain definitely the nature of the change at these inversion points, the solid, after it had remained in contact with the solution for several hours at different temperatures, was separated and analysed. In each case, the original solid, when brought into contact with the aqueous solution, was transformed into the trihydrate. The analysis was performed by converting the substance into barium sulphate as in the solubility estimations described below:

Temperature.	Percentage of barium.	
	Found.	Calculated.
0°	43.5	Trihydrate... 44.3
16	43.7	
27.4	50.0	Monohydrate 50.2
36.5	50.1	
49	53.6	Anhydrous... 53.7

These numbers show beyond doubt that, below the first transition point, the trihydrate is in equilibrium with the solution, whilst the anhydrous salt is in this condition above the second transition point,

the range for the stable existence of the monohydrate in contact with solution being limited by these two temperatures.

To establish the lower transition point more accurately, a fresh dilatometer was charged with trihydrate. From the previous dilatometric experiments and the above analyses we knew that the transition temperature probably lay between 20° and 27° . First, we found that there was a very pronounced increase of volume at 27° , so that this temperature was certainly above the transition point. At 22° , there was an equally pronounced diminution in volume, so that this temperature was as certainly below the transition point. At 24° , there was a slow but decided contraction; at 25.5° , a slow but decided expansion. The transition temperature therefore lay between these limits. Approaching the true inversion point from both sides, we ultimately found that at 24.5° there was a very slow diminution of volume, and at 24.8° a very slow increase in volume. At 24.7° neither expansion nor contraction could be observed. We may therefore conclude that 24.7° is the inversion temperature of the system trihydrate-monohydrate, the error in the determination probably not exceeding 0.1° .

Much greater difficulty was experienced in fixing accurately the inversion temperature of the system monohydrated-anhydrous salt. This was chiefly due to the comparative sluggishness of the transformation. Previous results had shown that the transition point lay somewhere in the range $35-45^{\circ}$, but a dilatometer charged with a mixture of monohydrate and anhydrous salt showed practically no change in volume at any temperature between 39° and 42° . We then endeavoured to increase the rate of the transformation by substituting a saturated solution of barium acetate for the toluene which we had previously used in the dilatometer. The bulb of a large dilatometer was filled with anhydrous salt in a fine state of division, heated at 50° , exhausted, and filled up with a solution of barium acetate saturated at the same temperature. The dilatometer was then placed in a thermostat at 39.3° . No very decided change was noted for some hours, but after a day it was observed that several crystals of monohydrate had begun to form. In the course of a week, these had become more than an inch in length, so that the dilatometer had to be broken in order that they might be examined. They proved to be crystals of the monohydrate, which rendered it certain that the temperature of the transition point was above 39.3° . At 40° , a similar growth of monohydrated crystals at the expense of the anhydrous salt was observed, and, although in this case the growth was much slower, there could be no doubt that the transition temperature was below 40° . At 42° , no change of anhydrous salt into monohydrate could be observed. On the contrary, a large crystal of the monohydrate, when

heated at this temperature in a test-tube containing xylene, in the course of a few days lost its transparency and showed distinct planes of cleavage. This behaviour indicated incipient transformation into anhydrous salt, and at a somewhat higher temperature the large crystal broke up into numerous small crystals about half a millimetre long, water being at the same time eliminated. The transformation at 42° was also confirmed by means of a dilatometer charged with monohydrate, anhydrous salt, and saturated solution, and this mixture showed a slight diminution in volume at 42° , that is, the volume change which accompanies the transformation of the monohydrate into anhydrous salt and water. The limits within which the second inversion point must lie are therefore $40-42^{\circ}$. We can consequently take 41° as the inversion temperature of the system monohydrated-anhydrous salt, with a liability to error probably not exceeding 1° . As will be seen later, the solubility data confirm this result.

Solubility Experiments.

The apparatus which we employed for determining the solubility of barium acetate was in all essentials identical with that described by Lumsden (Trans., 1902, 81, 352). At the higher temperatures, however, at which the solution was in contact with finely divided anhydrous salt, a different mode of filtration had to be adopted. During the process of saturation at these temperatures, the stirrer alone passed through the stopper of the bottle containing the solution. A second rubber stopper was provided with a filtering-tube and a short glass tube, which at one end was flush with the lower surface of the stopper, and at the other end was attached to the rubber tube of a hand-blower. The filtering tube was a capillary glass tube blown out at one extremity to a conical shape, a disc of filter paper supported between two discs of muslin being tied over the conical end. About half an hour before it was intended to filter off the solution, the stopper, fitted with the stirrer, was replaced by the stopper furnished with the filtering apparatus. The liquid was forced through the filter by means of the pressure produced by the blower; the first few drops were neglected, and then succeeding portions were delivered directly into the weighed platinum crucibles in which the composition of the solution was determined.

The crucible and its contents were weighed and the solution carefully evaporated to dryness. The evaporation during our first experiments was conducted on the water-bath, but it was found later that the concentration could be conducted much more rapidly and equally satisfactorily as follows. Two discs of asbestos millboard, 3 mm. in thickness, were placed on the bottom of a nickel crucible

about two inches in diameter, and on these the platinum crucible was laid, and then heated very gently by means of a small flame applied to the external nickel crucible. The evaporation proceeded rapidly and with little spirting, although, as a precautionary measure, the lid of the crucible was kept in position during the operation. There was no difficulty in weighing the residue of barium acetate as such; but to secure uniformity in the results the acetate was always converted into sulphate by the addition of concentrated sulphuric acid, the excess of which was driven off in the same manner, a larger flame being of course employed. The crucible containing the dry sulphate was finally heated directly by means of a Teclu burner.

As examples of the agreement obtained in the conversion of the acetate into sulphate, we may take the following. Two solutions, which on evaporation yielded residues of 1.0961 and 1.2522 grams of acetate, gave quantities of barium sulphate corresponding with 1.0969 and 1.2523 grams of the acetate respectively. The evaporation of the solution, conversion into sulphate, and ignition, did not by this method occupy more than an hour.

It was soon apparent after we had begun the solubility estimations that a time of contact, which would have ensured saturation in the case of most substances, was quite insufficient, in the case of barium acetate, to bring about equilibrium between the solid and solution. At low temperatures, the equilibrium between the solution and the trihydrate is established with moderate rapidity, but in the range of temperature including the transition points, and some way on either side, a considerable amount of difficulty was experienced in obtaining saturated solutions.

For example, at 16° the monohydrate after 1.5 hours gave a solubility of 69.0 parts of anhydrous salt in 100 parts of water. After 24 hours, the solubility obtained was 69.3, and after 48 hours, 69.2. The solution was thus practically saturated after one and a half hours' contact with constant stirring. On the other hand, at 41.8° the anhydrous salt after three hours' stirring gave a solubility of 76.7, which rose after 24 hours to 78.0. In every doubtful case we repeated our determinations of the solubility with constantly increasing times of contact until we obtained sufficiently concordant results. The following method gave good results for the anhydrous salt, with which we experienced most difficulty. A stock solution was prepared containing about 60 parts of anhydrous salt dissolved in 100 parts of water. This solution was heated at a temperature somewhat above that at which the determination was to be made, and then mixed with finely powdered anhydrous salt also heated at the same temperature. The solid and solution were vigorously stirred for about four hours, after which a fresh quantity of finely powdered

solid was introduced and the stirring continued for another hour. This seemed in every case to bring about saturation. In the majority of cases, parallel experiments were conducted with three bottles of solution in the thermostat in order to assure ourselves that equilibrium had been attained. In one of the bottles, the solid used was the trihydrate, in another the monohydrate, and in the third the anhydrous salt. For instance, at 39.6° , solutions saturated with the monohydrate as original solid gave a mean value for the solubility of 77.6; solutions which were saturated from the trihydrate gave 77.9, and solutions saturated from the anhydrous salt gave 78.2. Here the general mean value of 77.9 certainly represents the true equilibrium concentration with close approximation.

The following table gives our results for the solubility at different temperatures, each value being the mean of several concordant experiments. We are indebted to Mr. F. G. Young for the determinations at the four highest temperatures:

Temperature.	Parts $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ in 100 parts of water.	Solid in equilibrium with solution.
0.3°	58.8	$\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2, 3\text{H}_2\text{O}$
7.9	61.6	"
17.5	69.2	"
21.6	72.8	"
24.1	78.1	"
26.2	76.4	$\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2, \text{H}_2\text{O}$
30.6	75.1	"
35.0	75.8	"
39.6	77.9	"
40.5	79.0	$\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$
41.5	78.7	"
44.5	77.9	"
51.8	76.5	"
63.0	74.6	"
73.0	73.5	"
84.0	74.0	"
99.2	74.8	"

When these results are exhibited in curve form (p. 180), it is seen at once that we are dealing with three distinct curves, which intersect at points agreeing with the transition points determined by the dilatometer. Thus the curves for the two hydrates evidently cut each other at a temperature between 24° and 25° , corresponding with the transition point, 24.7° , previously found. Again, the curves for the monohydrate and anhydrous salt intersect at about 41° , in accordance with the estimate already given.

We made several attempts to obtain points on the curves in the metastable region beyond the transition points, but only met with success in the case of the lower transition temperature. At 26.1° , that is, about 1.4° above the first transition point, the transformation of trihydrate into monohydrate is comparatively slow, so that if the pure trihydrate is taken as the original solid, it is possible to obtain a solution considerably more concentrated than that corresponding with the number 76.3, which is the solubility of the stable monohydrate at this temperature. Thus the trihydrate after contact for three and five hours gave the solubilities 81.8 and 83.4 respectively, but after 22 hours' contact the solubility had sunk to 79.4. If we take the maximum number, 83.4, to represent the solubility of the metastable trihydrate, we find that in reality it falls on the prolongation of the trihydrate curve, as shown by the dotted line in the figure.

We were at first unable to secure a point on the monohydrate curve below the transition temperature, but at last succeeded by employing the following device. A porcelain mortar containing some finely powdered anhydrous salt was heated in a thermostat at 22° , and into this was introduced about 15 c.c. of a clear saturated solution of barium acetate at the same temperature. When intimately mixed with this solution by means of a pestle, the anhydrous salt was seen to dissolve freely, and after a few minutes the liquid suddenly began to deposit fine crystals of the monohydrate. It was then rapidly filtered and the concentration of the resulting solution ascertained. It was noticed that, before the analysis was made, the filtered solution deposited

a considerable quantity of the crystals of the trihydrate, thus showing that it had been supersaturated with respect to the trihydrate. The number obtained for the solubility was 81.0, which, it will be observed, lies accurately on the prolongation of the monohydrate curve below the transition point.

Krasnicki's Results.

It has already been mentioned that Krasnicki obtained results for the solubility of barium acetate which he was able to express with great accuracy by means of a single formula, that is, by a single curve. In order to show to what extent his results differ from our own, we have plotted his curve alongside those which give expression to our experimental data. Krasnicki makes no mention of the trihydrate, but states that barium acetate crystallises with one molecule of water, which it loses at 150°. His solubility experiments were apparently all conducted with the monohydrate as solid. For the attainment of equilibrium he allowed only from one to one and a half hours' shaking. In view of our own experience, this is altogether insufficient for the establishment of equilibrium at temperatures above 20°. Below that temperature, the results agree moderately well, above that temperature there is no further agreement except at about 47°, where the two curves intersect. It is remarkable that Krasnicki should have obtained concordant results from experiments made by heating and also by cooling solutions to the temperature at which saturation was desired, and further that his experimental results should diverge from those calculated from his formula by less than 0.1 per cent. in every case.

In order to test in a simple way between Krasnicki's results and our own, we saturated a solution at 100°, filtered, and allowed the clear solution to cool slowly. According to Krasnicki's curve, no solid would be deposited until the solution had cooled to at least 40°, and when once the solid had appeared, its quantity would constantly augment as the cooling proceeded. According to our curves, a small quantity of solid should appear after the solution had cooled only slightly, and this should then disappear at a temperature somewhere below 60°, no further solid appearing until the temperature had fallen to nearly 20°. What we actually observed was that crystals appeared in the solution when it had cooled to 84°. These crystals remained undissolved until the temperature had fallen to 49°, at which point the solution again became perfectly clear, to remain so until the room temperature was attained. No trihydrate had separated even after 24 hours, but the introduction of a minute fragment of this substance at once induced crystallisation. This experiment alone shows that Krasnicki's results for the higher temperatures are invalid.

Summary.

Dilatometric and solubility experiments show that the transition temperature from $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ to $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ is 24.7° , and that the transition temperature from $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ to $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ is 41° .

The solubility is not expressed, as Krasnicki found, by a single curve concave to the temperature axis, but by three independent curves, convex to the temperature axis, and intersecting at the transition points. The curve for the monohydrate shows a minimum at about 30° , and the curve for the anhydrous salt a minimum at about 75° .

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