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STUDIES IN THE HISTORY AND DEVELOPMENT OF THERMOGRAVIMETRY

II. Hannay's "Time Method"

C. J. Keattch and D. Dollimore

PO BOX 9, LYME REGIS, DORSET, DT7 3BT, U.K.
DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TOLEDO, TOLEDO, OH 43606, U.S.A.

James Ballantyne Hannay, born in Glasgow in 1855, was an outstanding Victorian scientist (see Appendix for a short biographical note). Although his scientific career was lamentably short, it has been described as a "period of creative activity which has rarely been exceeded in the history of science" [1]. R. H. S. Robertson, an authority on Hannay, regards his as one of the pioneers of thermal analysis [2], whilst no less an authority on thermal analysis than R. C. Mackenzie puts him in the same category as Le Chatelier as being one of the founders of thermal analysis [3].

Thus it seemed appropriate to consider Hannay's contributions to the development of thermogravimetry in some detail. In his work Hannay determined the loss in weight of a sample at regular time intervals on heating at a constant temperature [4, 5]. He referred to this technique as the Time Method which, by modern definition [6], is the method of Isothermal Weight Change Determination. A diagram of the apparatus is shown in Fig 1. Air is displaced from the large bottle (a) by water entering at (e). The air passes through the drying train (b, c) and over the sample spread in a thin layer at the bottom of a U-tube immersed in a bath (d), which is maintained at a constant temperature. In early experiments Hannay found that the drying tower (c), containing pumice soaked in "vitriol" had to be renewed after every determination. To obviate this tiresome chore, he introduced the drying bottle (b) containing "vitriol" and found that only this needed replac-

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* To whom requests for reprints should be made

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ing after every experiment. Since the large majority of the dehydration studies were carried out at temperatures of 100° or below, the bath (d) was filled with water and the temperature recorded by means of a bulb thermometer, as shown in Fig 1.

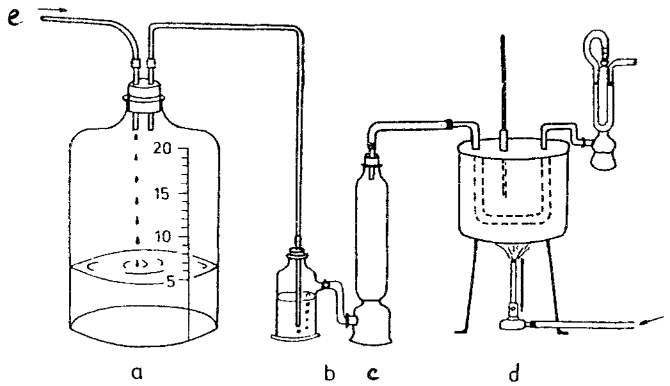

Fig. 1 Hannay's dehydration apparatus

Hannay first applied his "time method" to the study of gypsum [4]. Whilst recognizing the existence of $CaSO_4\cdot 2H_2O$, $CaSO_4\cdot\frac{1}{2}H_2O$ and $CaSO_4$, anhyd., he found that, in addition, the rate of water evolution pointed strongly to the existence of $CaSO_4\cdot 1\frac{1}{2}H_2O$, whereas the possibility of the formation of $CaSO_4\cdot H_2O$ could not be discounted. Hannay considered these results "as interesting as they are unexpected".

In the same publication, a detailed study of opal ($SiO_2\cdot H_2O$) and various synthetic hydrated silicas enabled Hannay to propose the existence of the following hydrates $6SiO_2\cdot 24H_2O$; $6SiO_2\cdot 6H_2O$; $6SiO_2\cdot 2H_2O$ and $6SiO_2\cdot H_2O$. In a more extensive study of various materials [5], he suggested the existence of several new compounds. For example, $Na_2SO_4\cdot 2H_2O$ and $Na_2SO_4\cdot H_2O$ were identified in addition to the well established hydrates $Na_2SO_4\cdot 10H_2O$ and $Na_2SO_4\cdot 7H_2O$. Similarly, the existence of $MgSO_4\cdot 3H_2O$ and $MgSO_4\cdot 2H_2O$ were proposed, in addition to the well-known hepta-hexa- and monohydrates. The tri- and dihydrates were confirmed, much later, by Heide [7], using conventional thermogravimetry, although more contemporary and detailed studies [8] suggest that $MgSO_4\cdot 2H_2O$ is metastable. A new hydrate of zinc sulphate $ZnSO_4\cdot 3H_2O$ was also suggested. No new hydrates were found during the dehydration of $FeSO_4\cdot 7H_2O$ because, says

Hannay, "the loss of the first five molecules of water was to rapid to detect the formation of any new compounds".

Hannay also re-examined $CaSO_4 \cdot 2H_2O$, this time as selenite, in order to determine accurately the dissociation of the previously postulated hemihydrate ($CaSO_4 \cdot 1\frac{1}{2}H_2O$). He maintained finely powered samples for 20 minutes at 100°, 103°, 105°, 110°, 115° and 117° and found no weight loss. However, at 118° water began to be evolved and after about two hours at 125°, 15.28% water had been evolved, but a temperature of 150° was necessary to complete the first stage of the decomposition, when 15.68% of water had been expelled, the calculated amount for the reaction:

$$CaSO_4 \cdot 2H_2O \xrightarrow{-H_2O} CaSO_4 \cdot \tfrac{1}{2}H_2O$$

being 15.69%. On further increasing the temperature and weighing at intervals, it was found that dehydration was complete at 190°. Hannay also found that if, when decomposition commences at 118°, the temperature is lowered to 100°, decomposition still proceeds, or rather, as he says "at that temperature at which the vapour-tension of water equals the pressure of the atmosphere, because 15% of the water of calcium sulphate may be expelled at 99° (after starting at 118°) provided the barometer be at such a height that this is the temperature of boiling water". The graphs drawn by Hannay of the mass loss *vs.* time indicate a compound having the formula $CaSO_4 \cdot \frac{1}{2}H_2O$, whereas there is not the slightest indication of the existence of $CaSO_4 \cdot H_2O$. This work on gypsum indicates the important role played by the partial water vapour pressure in the thermal decomposition of the $CaSO_4-H_2O$ system. For example, later work by Jolibois and Lefebvre [9] showed that either heating 0.5g samples in an open crucible under dynamic heating conditions or maintaining 0.5g sample sat constant temperature in the range 60-130° did not differentiate between the di- and hemihydrates, whereas maintaining a 3g sample at 141° in a covered crucible, mass losses were obtained which approximated to the formula $CaSO_4 \cdot \frac{1}{2}H_2O$.

More recent work [10] showed that on heating small sample (~0.3g) over a fairly wide temperature range (0.5–6 deg/min) it was not possible to differentiate between $CaSO_4 \cdot 2H_2O$ and $CaSO_4 \cdot \frac{1}{2}H_2O$, whereas maintaining the temperature of similar sample sizes at 90-93°, resulted in a mass loss from the dihydrate equivalent to $1\frac{1}{2}$ molecules of water and subsequently increasing the temperature to 160° caused a further mass loss equal to the remaining half molecule of water.

In the two more recent examples cited above [9, 10] it is quite apparent that sample size is of considerable importance. It is regrettable that Hannay never gives the mass of samples used, invariably merely stating "a quantity weighed out". At the beginning of the paper discussed above [5], Hannay mentions his friend Ramsay's (Sir William) interest in the time method and that he had suggested the technique may be profitably employed in studying the decomposition of amorphous hydrates. Consequently, it was agreed that Hannay studied crystalline hydrates and Ramsay amorphous compounds, the topic being divided in this manner since they were working in different laboratories, Ramsay as assistant to Prof. J. Ferguson, Professor of applied chemistry, and Hannay as senior assistant to Prof. W. Dittmar, "Young" Professor of technical chemistry, both at Anderson's College Glasgow [11].

As would be expected, results on the amorphous hydrates, were less easy interpret. For example, Ramsay was only able to postulate the existence of hydrates such as $Al_2O_3 \cdot 4H_2O$, $Al_2O_3 \cdot 3H_2O$ and $Fe_2O_3 \cdot 3H_2O$. He was, however, more fortunate with his work on copper and lead hydrates in that he was able to confirm, with confidence, the existence of $CuO \cdot H_2O$; $3PbO \cdot H_2O$ and $2PbO \cdot H_2O$ [12].

These few interesting papers are the sum total of work on the Time Method by Hannay and Ramsay and the topic was not pursued by any of their contemporaries. Largely as a result of Robertson's influence, [2] interest in Hannay's Time Method has recently been revived and work is currently in progress on the $CaSO_4-H_2O$ system, using the same basic apparatus but more sophisticated measuring techniques [13].

Appendix

James Ballantyne Hannay was born on 1 January, 1855 at No 1, Kelvingrove Place, Glasgow. Before he was 10 years old he took an interest in chemistry, reading books on the subject and attempting to repeat some of the experiments described therein, in a laboratory which he set up in his home. His formal education was obtained at Larchfield Academy, but he disliked school and left at the age of 14.

In 1872 he was elected a Fellow of the Chemical Society and in 1873 joined a firm of bichromate manufactures in Glasgow, leaving in 1876 due to ill-health, having attained the position of works manager. Also in 1876 he became a Fellow of the Royal Society of Edinburgh and sometime later was elected a Fellow of the (then) Institute of Chemistry.

In addition to being a successful businessman, he was also a brilliant experimentalist and glass blower. His scientific papers and patents covered a wide range of topics, probably the best known being the highly controversial synthetic "Hannay Diamonds". A lifelong friend of Sir W. Ramsay he abandoned his scientific pursuits later in life in favour of religion. He died on 17 March, 1931.

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