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**THE ROLE OF THERMAL ANALYSIS IN MINERALOGICAL
STUDIES. PART III. HANNAY'S EXPERIMENTS
IN EVOLVED GAS ANALYSIS, 1876—1879**

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Abstract. James Ballantyne Hannay (1855—1931), who made accurate measurements by evolved gas analysis in train with isothermal and isobaric weight loss techniques, may be regarded as a major pioneer of thermal analysis before Le Chatelier's improvement of the thermocouple in 1836. Hannay's "time method" and use of very dry air are recommended for investigating different states of water in clays and other substances since the method is more sensitive than many thermal analytical techniques in use today.

INTRODUCTION

James Ballantyne Hannay (1855—1931) had to leave Scotland in the Spring of 1876, his health having suffered from chromium poisoning in a Glasgow factory. Yet within a year he had returned and begun a period of creative activity, which has rarely been exceeded in the history of science (Flint, 1968). He was the first to show that the magnetism of rocks was due to the presence of discrete particles of magnetic minerals; he described several new minerals; he designed an easily-made reflecting goniometer; his work on the cohesion (viscosity) of liquids and the design of his microrheometer made him one of the "Fathers of Rheology"; and his work on the solubility of solids in gases above the critical pressure place him among the greatest experimentalists of his time.

In the history of thermal analysis he has been remembered as the inventor of the method known as isothermal weight change determination (Keatch, 1976), following Mackenzie (1969), who later (in "De Calore", in preparation) felt that Hannay and William Ramsay and possibly Henri Victor Regnault, should be regarded, along with Le Chatelier, as Founders of Thermal Analysis. While differential thermal analysis natu-

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rally followed from La Chatelier's perfection of the thermocouple in 1886, we can now recognise that Hannay introduced both isothermal and isobaric weight change determinations and is also responsible for first carrying out evolved gas analysis — from 1876.

THE TIME METHOD

Hannay's "Time Method" was to cause air, by means of an aspirator, to bubble through several vessels containing sulphuric acid and, when necessary P_2O_5 as well, in order to make a supply of very dry air. A thin layer, about 1 mm deep, of a hydrated substance was placed in a tube suspended in a heated water- or oil-bath. The dried air was passed above the substance and the water vapour evolved was collected in two U-tubes containing pumice saturated with sulphuric acid, one being attached to the instrument while the other was being weighed; by these means the dehydration was kept going constantly. Weighings were done every 5 minutes at first and then at longer intervals when the rate became slower. We now call this technique evolved gas analysis.

HYDRATED SALTS

Hannay showed that a salt which refuses to give up its moisture at $100^\circ C$ in ordinary air may do so in very dry air, and referred to the well-known phenomena of efflorescence and deliquescence. He could say from his experiments that the rate of dehydration is not a measure of the vapour-tension of the water in compounds, but a measure of the difference between such tension and that of the moisture in the air employed; but where this is extremely small compared with that in the salt, the time of dehydration may be considered as a direct measurement of the vapour-tension.

In his most important paper on the "Examination of Substances by the Time Method" (1877) he illustrates the apparatus (fig. 1) he used and gives results of runs with hydrated salts. Sharp inflexions in the weight loss/time curves indicated several new hydrates of Fe^{2+} , Na, Mg, and Zn sulphates; on the other hand, several hydrates prepared in a variety of ways by previous workers, did not show as discontinuities.

He showed that at low temperatures more hydrates are formed or are indicated by this method than at high temperatures; and that, if the temperature were raised high enough, all sudden changes in vapour-tension would be eliminated, as they are in differential thermal analysis, for example.

It was possible to discriminate between hygroscopic moisture and chemically combined water, as in opaline silica (Robertson, in press) and between moisture regained when a partially dried substance is in contact with moist air. The regained moisture is lost more quickly than the hydrate water.

While the vapour-tension of lower hydrates is usually less than that of the higher hydrates, but in zinc sulphate heptahydrate the opposite was the case over much of the drying curve.

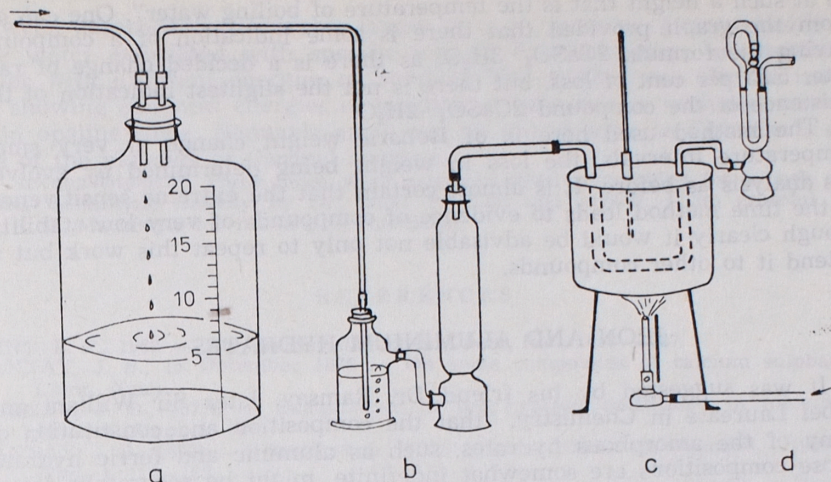


Fig. 1. Hannay's dehydration apparatus
a — aspirator, b — drying train, c — water or oil bath, d — drying vessels

GYPSUM

"An examination of calcium sulphate by this method gave results pointing to the existence of the compound $2CaSO_4 \cdot 3H_2O$. In examining this compound, experiments had to be made to determine accurately its dissociating point. It is generally stated that calcium sulphate gives off three-fourths of its water between 100° and 120° , and does not part with the last portion till between 200° and 300° . A weighed portion of pure selenite, finely powdered, was submitted to the following experiments: It was kept for 20 minutes at each of the following temperatures, without suffering any loss — 100° , 103° , 105° , 110° , 115° , 117° but at 118° water began to come off, and after about 2 hours at 125° , it had parted with 15.28 per cent of its moisture; but it required a temperature of 150° to complete the first stage of the decomposition, when 15.68 per cent had been expelled, the calculated amount for $2CaSO_4 \cdot 4H_2O - 3H_2O$ being 15.69.

The temperature was then raised and weighings made at intervals till it was found that the last stage of the decomposition began at 178° . The temperature was maintained at 180° for an hour, when it was found that 19.78 per cent had been driven off. As the dissociation had ceased, the temperature was raised to 190° , when after 30 minutes, the loss was 20.78, the calculated amount being 20.93. Thus we find that calcium sulphate may be entirely dehydrated at 190° . It was further noticed that when the first dissociation is started at 118° , if the temperature be lowered, the decomposition still goes on even at 100° , or rather at that temperature at which the vapour-tension of water equals the pressure of the atmosphere, because 15 per cent of the water of calcium sulphate may be expelled at 99° (after starting at 118°), provided the barometer

be at such a height that is the temperature of boiling water". One can see from the graph provided that there is some indication of a compound having the formula $2\text{CaSO}_4 \cdot 3\text{H}_2\text{O}$, as there is a decided change of rate after 5.53 per cent of loss, but there is not the slightest indication of the existence of the compound $2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

The method used here is of isobaric weight change at very small temperature intervals, the loss in weight being determined by evolved gas analysis as before. It is almost certain that the extreme sensitiveness of the time method leads to evidence of compounds of very low stability, though clearly it would be advisable not only to repeat this work but to extend it to other compounds.

IRON AND ALUMINIUM HYDRATES

It was suggested by his friend Dr. Ramsay, later Sir William and Nobel Laureate in Chemistry, "that the composition and constitution of many of the amorphous hydrates, such as aluminic and ferric hydrate, whose compositions are somewhat indefinite, might be accurately determined by this method, as the vapour-tensions of hygroscopic and combined water would differ so much that a definite distinction could be made between them". They accordingly divided the research work between them, Dr. Ramsay doing his work at Glasgow University, Hannay in his own laboratory.

Ramsay says "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". We see that Ramsay did not dry the air, did not specify a thin layer of powder and measured the isobaric weight loss at large temperature intervals. It is not perhaps surprising that he found evidence only of the monohydrates, $\text{AlO} \cdot \text{OH}$ and $\text{FeO} \cdot \text{OH}$, but not of the trihydrates. Moreover he did not compare the precipitated hydrates with any natural minerals.

In view of the relatively crude experimental technique used by Ramsay and the fact that Hannay had used both isothermal and isobaric weight change techniques, I would suggest that Ramsay need no longer be considered as one of the pioneers of thermal analysis. He caught some of Hannay's enthusiasm for the subject but failed to add anything to it. Hannay's place however seems assured by the following consideration: one cannot build upon Ramsay's work in this field, but one can do so on Hannay's.

CONCLUSION

Now that evolved vapours can be continuously and automatically determined in modern apparatus, there is no reason why Hannay's method of passing very dry air at different temperatures over hydrated materials should not be brought up to date and used for distinguishing

between adsorbed water, water layers — such as those in montmorillonite water associated with specific ions in homionic clays and zeolitic water with different energies of bonding. The method can also be used for showing different energies of bonding of adsorbed or occluded water, as in opaline silica. Hannay's name can be linked with Le Chatelier's as one of the pioneers of thermal analysis.

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ZNACZENIE ANALIZY TERMICZNEJ W BADANIACH MINERALOGICZNYCH. CZĘŚĆ III. DOŚWIADCZENIA HANNAY'A W ZAKRESIE ANALIZY WYDZIELANEGO GAZU

Streszczenie

Praca opisuje doświadczenia jakie przeprowadzał James B. Hannay wykonując dokładne pomiary wydzielanego gazu w układzie izotermicznej i izobarycznej utraty wagi. J. B. Hannay może być uważany za głównego pioniera analizy termicznej — zanim jeszcze Le Chatelier udoskonalił termoparę w 1886 roku. Metoda „czasowa” Hannay'a i stosowanie wysu-

szego powietrza są zalecane do badań różnych stanów wody obecnych w minerałach ilastych i innych substancjach. Metoda ta jest bardziej czuła niż pozostałe techniki termicznej analizy obecnie stosowane.

OBJASNIENIE FIGURY

Fig. 1. Aparat odwadniający Hannaya

a — pochłaniacz, *b* — układ suszenia, *c* -- kąpiel wodna lub olejowa, *d* — naczynia odwadniające

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ЗНАЧЕНИЕ ТЕРМИЧЕСКОГО АНАЛИЗА В МИНЕРАЛОГИЧЕСКИХ ИССЛЕДОВАНИЯХ. ЧАСТЬ III. ЭКСПЕРИМЕНТЫ ГАННЕЙА КАСАЮЩИЕСЯ АНАЛИЗА ВЫДЕЛЕННОГО ГАЗА

Резюме

В работе описаны эксперименты, которые выполнил Дж. Б. Ганней производя детальные измерения выделенного газа в системе изотермической и изобарической потери веса. Дж. Б. Ганней считается пионером термического анализа. Он проводил исследования еще до того когда Ле Шателье усовершенствовал в 1886 году термопару. „Временный метод Ганнейа и применение высушенного воздуха рекомендуется для исследований разных состояний воды присутствующей в глинистых минералах и других субстанциях. Этот метод более чувствителен чем остальные применяемые техники термического анализа.

ОБЪЯСНЕНИЕ ФИГУРЫ

Фиг. 1. Обезвоживающий аппарат Ганнейа

a — поглотитель, *b* — система высушивания, *c* — водная или масляная промывка, *d* — обезвоживающее устройство