A SILICA SPIRAL THERMO-BALANCE FOR STUDIES ON THE DEHYDRATION OF CLAY MINERALS

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ABSTRACT

Constructional details of the balance and methods to give maximum sensitivity in obtaining and presenting results are described. Examples of work on clay minerals include comparison of results from the balance with d.t.a. traces of kaolinite and halloysite, low temperature dehydration of various montmorillonites, and a series at different rates of heating showing the relation between the d.t.a. trace and the equilibrium isobaric dehydration curve of Li⁺-Wyoming bentonite.

INTRODUCTION

The apparatus described in this paper is not a new one, as the use of a silica spiral for a balance was first described by McBain and Bakr (1926). However, as these spirals are now easily obtained, the suggestion is made that a simple balance of the sort described, using existing control mechanisms, should be used to give additional data as an accompaniment to d.t.a. curves.

This paper is in two parts; the first describes the apparatus and its method of operation, and the second shows results for some clay minerals which have been selected to show the possibilities of the balance.

DESCRIPTION OF APPARATUS

Fig. 1 shows a sketched elevation of the instrument. The fused silica spiral (1) is obtained from Thermal Syndicate Ltd., and has a maximum load of 500 mg. The platinum bucket and suspending wire together weigh 130 mg, and a 100 mg sample of clay is normally used. Initially the spring is calibrated using weights of from 50-150 mg in the bucket, Hooke's Law being obeyed over this range. When the 12 mg calcite rhomb was used, Fig. 4e, platinum weights were added to adjust the bucket position in the furnace, and to enable the sample to be weighed in the calibrated range.

Sensitivity. The cathetometer (11) is focussed on to the lower loop of the spiral and can be read to 0.002 cm, which corresponds to 0.05 mg or 0.05% of a 100 mg sample. A pyrex glass spine (12) is
used as a zero point for readings and also as a check against expansion of the balance case during heating.

The bucket (2) is of platinum, with a capacity of 0.3 ml and holds 100 to 200 mg of clay. It is suspended by a platinum wire, diameter 0.002 inches, and located in an even temperature zone in the furnace. Buoyancy corrections for the bucket and sample are not necessary. The displacement of the bucket is negligibly small, and 100 mg of clay occupy approximately 0.04 ml and the weight of air displaced is therefore 0.05 mg at 0°C, so that the maximum correction will be less than the experimental error of the cathetometer readings.

The Balance Case. The top cap (3) is of brass with three centring screws and a central hook on which the spring and spine are sealed with black wax. The main case (4) is a pyrex tube, 4.5 cm in diameter and 30 cm long, which is cemented with litharge cement into the lower brass holder. The latter consists of a water-cooled jacket
(5) and two vanes (6) to cut off direct radiation from the furnace on to the spring. The vanes are effective to at least 900°C and are important as the elasticity of the spiral is temperature dependent.

*The thermo-couple* (7) is of chromel-alumel wire sheathed in a silica tube led through the lower brass section of the case. The bare hot junction is placed as close as possible to the sample and in a vertically even temperature zone in the furnace. Temperatures are recorded on a Kent Recorder. A tube to supply nitrogen (8) at a known humidity to the furnace is also fitted, but in the examples shown in this paper no attempt was made to control the humidity in the furnace.

*The Furnace* (9) is made from a closed silica tube 15 cm long and 2.5 cm in diameter. The heating coil is Nichrome V resistance wire wound round the tube to give a resistance of 60 ohms. The furnace is lagged with alumina furnace sand poured into the asbestos case, and thermally insulated on top by another water-cooled jacket (10). The balance case and furnace are clamped to leave a small air gap when operating, so that expansion of the furnace does not affect the cathetometer zero.

**Furnace Control.** The furnace current comes from a motor-driven variac transformer. Two methods of control have been used: (1) The Kent programme controller operates a “high-low” switch 5 volts apart on the transformer and a cam controls the rate of heating. This method can never be really satisfactory as it involves two separate rates of heating applied alternately. (2) When working at 3°C per minute no cam was available, and manual control was used. A line was drawn on the recorder chart at the correct slope for the required heating rate, and the temperature trace kept to the line by advancing the motor and variac at intervals. With practice this method can give results as accurate as the recorder is capable of showing, but furnace control is undoubtedly one of the limits to the accuracy of the results obtained.

**Recording Changes in Weight.** Two methods have been used: (1) For reading at 10°C intervals the cathetometer is set on the lower loop of the spring and the scale reading recorded. (2) For shorter time and temperature intervals the cathetometer is set successively at positions 0.1 mm apart, and the coincidence of the spring and cross-wire timed with a stop-watch. Temperatures from the chart are also recorded and the temperature of each reading calculated afterwards. If a linear rate of heating is maintained, the errors from the individual
readings are not cumulative. Two operators are required for this method, but intervals as small as ten seconds can be measured satisfactorily.

Presentation of Results. The cathetometer readings and time in seconds are first calculated and plotted to give change of weight against temperature. This type of curve is familiar from equilibrium water-loss studies. A useful addition to this when the curve is well defined with a large number of points is the derivative curve of rate of change of weight against temperature. This corresponds to a d.t.a. trace in shape and forms a useful comparison. It must be emphasised that a derivative curve accentuates errors, and if the peak shapes and temperatures are to mean anything the original data must be accurate. Two satisfactory methods have been used to evaluate the derivative curve, a third in which tangents were drawn by placing a straight-edge to the curve at successive points was not reproducible to better than 10%.

METHOD 1. Use is made of an equation for numerical differentiation (Hartree 1952). The data obtained from experimental runs consist of time intervals, in seconds, for equal increments in cathetometer readings, and the reciprocals of the results are taken to be proportional to the tangents of the curve at the point in question. The equation has been programmed for the Elliot electronic computer at Rothamsted, and this method has the advantage that no personal interpretation is involved in obtaining the derivative curve. Figs. 4 (b), (d), and 6 (b), (c) show this method in use, and Fig. 2 shows the effect of 1, 3 and 5-point smoothing. Note the distortion introduced by 5-point smoothing at points where the original weight loss-temperature curve has a rapid change of slope.

METHOD 2. As seen in Fig. 3 the results of the cathetometer readings and time in seconds are drawn on a large scale. A suitable time interval, 40 sec in the example but usually 100 or 120 sec, is selected and the vertical separation corresponding to it is measured for each point, \( \delta_1, \delta_2, \delta_3 \) etc., by counting squares. The values are thus directly proportional to the tangent of a chord of arc, but are plotted directly to give the derivative curve. If the time interval selected is long, it can be seen that the result will show distortion similar to that given by 5-point smoothing in the previous method. Figs. 4 (b), (d), (e), 5 and 6 (c), (d), show Method 2 in use, it is rapid and seems to be quite satisfactory.

In the diagrams shown, no ordinate scale is given for the derivative curves or d.t.a. traces. The reason for this is that the units used are
Fig. 2—Li⁺-Wyoming bentonite heated at 10°C per minute. Derivative curves (rate of loss of weight against temperature) obtained using Hartree's equation, Method 1, and showing how peak shape is modified by smoothing. Upper 5-point smoothing, middle 3-point smoothing, lower 1-point smoothing.

Fig. 3—Derivative curves obtained by method 2. $\delta_1, \delta_2, \delta_3$ are plotted against temperature.
quite arbitrary, but are in fact comparable with each other. It would have been possible to give the Method 2 derivative curves, in rate of water loss in milligrams per gram of dehydrated clay for a 10°C rise in temperature, but the considerable work involved hardly seemed justified.

Spring Oscillation. At temperatures between about 90°C and 800°C, a small damped oscillation of the lower end of the spring is obtained. This is sufficiently intermittent to allow accurate readings in general, but can interfere on runs at 10°C a minute when the spring is travelling quite quickly past the cross-wire. The oscillation is not affected by substitution of a needle or a flat horizontal disc for the bucket, and does not appear to be due to radiation as it starts at about 90°C and disappears again at 800-900°C, hence its origin is still unsolved. However, if, as is suspected, the oscillation is due to circulating convection currents, it is hoped that improved furnace design will eliminate this disturbance.

APPLICATION TO CLAY MINERAL STUDIES.

The following examples have been selected to demonstrate the sensitivity, accuracy, performance at high temperatures, and the way in which the balance can be used to supplement information given by d.t.a. traces. Figs. 4 (a) and (c) show d.t.a. traces of B.L.I. kaolin and halloysite from Eureka, Utah. The traces were made at a high chart speed and then expanded so that the temperature scale coincided with that used in plotting the micro-balance curves. Figs. 4 (b) and (d) show the results on the same materials, made on the micro-balance at the same heating rate of 10°C per minute. The derivative curves have been drawn by each of the methods described earlier so that the results may be compared. In each of the d.t.a. traces the peak temperatures were checked using an internal standard of \( \text{K}_2\text{SO}_4 \) or AgI as suggested by Barshad (1952). The d.t.a. traces of the kaolinite and halloysite on equal quantities of material are on the same vertical scale. The similarity between d.t.a. traces and the weight-loss—temperature derivative curves for each of the materials can be seen. The difference in the slope ratios of the peaks of kaolinite and halloysite, pointed out by Bramao, Cady, Hendricks and Swerdlow (1952) on d.t.a. traces of similar materials, is also obvious. When the peaks are expanded in this way, however, the method of obtaining slope ratios has considerable importance.

Fig. 4 (e) shows the weight loss-temperature curve of a rhomb of calcite, heated at 10°C per minute, and its derivative curve. It is
Fig. 4—Samples heated at 10°C per minute. +++ lattice water-temperature curve. ... derivative curve (rate of loss of weight-temperature)

(a) expanded d.t.a. trace of B.L.I. kaolin, showing endothermic peak,
(b) thermo-balance curves of B.L.I. kaolin, showing the endothermic peak,
(c) expanded d.t.a. trace of halloysite, Eureka, Utah, showing the high temperature endothermic peak,
(d) thermo-balance curves of Eureka, halloysite,
(e) thermo-balance curves of a calcite rhomb, for comparison with halloysite, sample weight 12 mg. (+++ CO₂—temperature curve)
interesting to note that this simple reaction (Britton, et alia 1952) in which the rate is proportional to the area of the reacting interface gives a markedly asymmetrical derivative curve. This is analogous to that obtained with halloysite, but quite different from that of kaolinite. In this run the sample taken weighed 12 mg, and the total loss of CO₂ was within 1% of the theoretical amount, although no particular attempt was made to obtain accuracy.

The remaining traces show the low temperature dehydration of montmorillonite. The samples, with one exception, were prepared by equilibrating over a free water surface and then over a solution giving a relative humidity of 20% at 25°C. For Li⁺-Wyoming bentonite at 10°C per minute the material was prepared at 7% R.H.

A useful check on the resolution of a d.t.a. apparatus, is to find if it is possible to resolve the two components of the low temperature endothermic peaks of Ca²⁺-Wyoming bentonite. The microbalance can hardly distinguish the high temperature component of the peak for this material when operating at 10°C per minute, although Fig. 6 (b) shows that it can for the Li⁺-saturated mineral. Part of the reason for this, is that the water associated with this peak comes off in a very small time interval, and the effect is made uncertain by considerable random error of a single reading. When the heating rate is reduced the resolution is improved and better detail can be obtained. A rate of 3°C per minute was selected as it is easily controlled and gives runs of a suitable duration. Figs. 5 and 6 (b) of runs at 3°C per minute show results at maximum sensitivity. The low and high temperature components of the complex peaks are clearly resolved, and differences in the peak shape between the Ca²⁺ and Li⁺-montmorillonites can be seen.

Na⁺-Wyoming bentonite, (Fig. 5 (d)), and Na⁺-Unterrupsroth, a material described by Nagelschmidt (1938), show only a single peak and the shape is similar to that obtained for calcite at 10°C per minute, and similar also to the high temperature component of the Li⁺, but not Ca²⁺ montmorillonites. These curves cannot be compared directly with the d.t.a. traces as the rate of heating is different, but in Fig. 6 the derivative curve for Li⁺-Wyoming bentonite and the d.t.a. trace for the same material at 10°C per minute are given. Successive curves show the relationship between the d.t.a. trace and the equilibrium isobaric dehydration curve for the same material, in which readings at 10°C intervals were taken every 48 hours. These curves demonstrate that the features found in the d.t.a. traces are to an extent independent of heating rate and appear on the isobaric equilibrium curves, from which they are best studied.
Fig. 5—Low temperature dehydration in montmorillonite. Samples heated in the thermo-balance at 3°C per minute and showing maximum detail. The samples were prepared by equilibrating over a free water surface, and then at 20% relative humidity at 25°C. +++ inter-lattice water-temperature curves. . . . derivative curves.
(a) Ca²⁺-Wyoming bentonite, (b) Ca²⁺-Unterrupstroh montmorillonite, (c) Li⁺-Unterrupstroh montmorillonite (duplicate runs are shown), (d) Na⁺-Wyoming bentonite.
Fig. 6—Effect of rate of heating on dehydration curves of Li\(^{+}\)-Wyoming bentonite. +++ inter-lattice water-temperature curves. ... derivative curves.

(a) heating rate 10°C per minute, expanded d.t.a. trace low temperature endothermic peak, (b) heating rate 10°C per minute, thermo-balance curves, (c) heating rate 3°C per minute, thermo-balance curves, derivative curves; upper—graphical, method 2, lower—computer, method 1, (d) heating rate 5°C every 15 minutes, thermo-balance curves, also two sets of readings every minute show the approach to equilibrium. (e) heating rate 10°C every 48 hours, equilibrium isobaric dehydration, water vapour pressure 24 mm Hg.
The object of this paper has been to demonstrate the accuracy, sensitivity, and ease of working of the micro-balance. The traces illustrating these features also raise a number of questions on the nature and mechanism of the dehydration of these minerals. No attempt has been made here to answer these questions as it is intended to deal with them separately at a later date.

The advantages of the silica-spiral balance as a complementary technique to d.t.a. are as follows:
1. It is cheap and simple to make and can use existing control and recording systems.
2. It uses a small sample; 100 mg is adequate.
3. The information given is specific, i.e., loss of weight, whereas d.t.a. information is inferred.
4. Under similar conditions the sensitivity is comparable with that of the d.t.a., and by reducing heating rates the connection can be shown between d.t.a. and equilibrium dehydration conditions.
5. The balance and d.t.a. together will distinguish between peaks due to loss in weight and endothermic peaks due to phase changes in the minerals. In soil clays the combustion of organic matter gives a large exothermic drift on the d.t.a. and this often distorts the trace over a wide range of temperature. In the balance the only effect is a small loss in weight.

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