THERMOGRAVIMETRIC ANALYSIS OF CLAY AND CLAY-LIKE MINERALS

By

RICHARD C. MIELENZ, N. CYRIL SCHIELTZ
and MYRLE E. KING
Petrographic Laboratory, Bureau of Reclamation, Denver Federal Center,
Denver, Colorado

ABSTRACT

The thermogravimetric method offers a new approach to the study of clay and clay-like minerals as well as other minerals and compounds that gain or lose weight upon heating. This method is complementary to differential thermal analysis, which records energy gains or losses upon heating. Thermogravimetric curves for clay and clay-like minerals are presented and correlated with curves obtained by the differential thermal method. The apparatus, procedures, limitations, and application of the method are described and illustrated.

INTRODUCTION

Differential thermal analysis has proved to be of great value for identification and study of the properties of clay and claylike minerals. However, as is well known, this method depends upon the release or absorption of heat by the sample during the temperature cycle, and these transformations of energy result from either loss of volatile components or changes of entropy with reorganization of atomic structures in the sample. It is therefore of value to introduce a method whereby changes of weight of a sample can be determined directly and contemporaneously with heating, so as to distinguish the two types of energy change.

Ideally, thermogravimetric and differential thermal measurements should be carried out simultaneously on the same sample. Apparatus designed to do this is now being developed at the National Bureau of Standards. A differential thermal balance which emphasizes changes in rate of weight loss or gain by the sample was described recently by DeKeyser (1953, p. 364).

A thermal balance designed by Chevenard, Waché, and de La Tullage (1944) was manufactured for sale in France in 1947. Its commercial availability in the United States was announced in an article by Duval (1951, p. 1273). The Chevenard thermal balance was designed for the investigation of dry corrosion of metals, but was applied more generally by Duval (1951, 1953) to studies in analytical and physical chemistry.

Our instrument, delivered in February 1953, has been used primarily in study of clay and clay-like minerals in conjunction with differential thermal analysis. This paper summarizes our observations, especial emphasis being given its use, its precision, and the reproducibility of results.

THE THERMAL BALANCE

General Statement

The thermal balance used in these investigations was developed by Chevenard, Waché, and de La Tullage (1944) and is manufactured by the Société A.D.A.M.E.L. (Atelier d'Appareils de Mesure et de Laboratoire) Paris, France.

The apparatus permits continuous weighing and recording of changes in weight of a reaction system involving solid, liquid, or gas, in air or in a controlled atmosphere, during heating at selected rates from room temperature to 1,050° C, or at constant temperature in this range. The thermal balance accommodates samples weighing 100 mg to 10 g (including the sample holder) and is capable of indicating weight changes (gains or losses) up to 400 mg. The sensitivity is adjustable and such that a change of 100 mg in the weight of the sample will produce a deflection of 50 to 60 mm in the recorded trace of the time-weight curve. Deflections of the curve are approximately proportional to the weight change.

Only a brief description of the Chevenard Thermobalance No. 102 is given here. More detailed information can be obtained from publications of Duval (1951, 1953). The notes on performance are based upon our experience with the instrument in our laboratory.

The thermal balance comprises three essential parts: (1) the balance, (2) the furnace and controls, and (3) the recording system (Fig. 1 and Pl. 1).

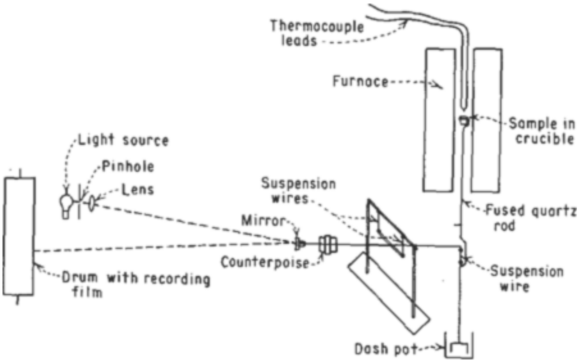

FIGURE 1. — Diagram of the Chevenard thermal balance, model no. 102.

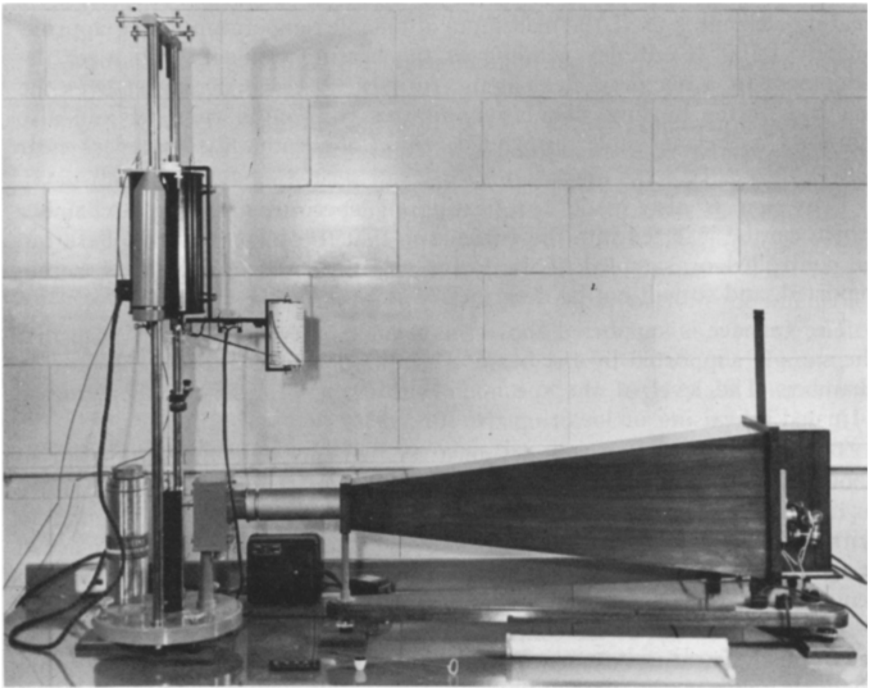

PLATE 1. — The Chevenard thermal balance, model no. 102.
Furnace and control drum at left above; balance in housing at left below; housing for light source and recording device at right.

The Balance

The balance is designed to weigh continuously specimens of various types while the specimen is within a furnace and is being heated or cooled, or is maintained at an elevated constant temperature. The beam of the balance is of Duraluminum, 23 cm long, and supported by two tungsten wires. Each wire is 0.05 mm in diameter and 25 mm long. The sample is supported above the balance by a vertical rod which is counterbalanced and suspended from the beam by a tungsten wire. The weight of the suspension system supporting the sample is balanced by an adjustable counterpoise on the beam. The end of the beam opposite from the end supporting the sample carries a mirror 9 mm in diameter for reflecting an incident light beam to the recording device.

The Furnace and Controls

The furnace is cylindrical in form and is of the electrical resistance type, operating on 110 to 115 volts. The axis of the heating chamber is vertical when the furnace is mounted in its supports. A nickel-chrome heating element is used, the maximum attainable temperature being approximately 1,100° C. Bifilar winding of the heating elements minimizes development of a magnetic field in the furnace. A ceramic cap set over the top end of the heating chamber minimizes convection currents and also supports a thermocouple suspended within a sheath of silica glass near the sample.

Provision is also made for heating of specimens within a chamber which can be inserted into the furnace so that the furnace atmosphere can be controlled or sampled. This device was not used in the study herein reported, and so will not be described.

The furnace is supported above the balance by two steel posts such that the sample supported by the beam is centered on the axis of the heating chamber. The level of the specimen within the heating chamber can be adjusted by raising or lowering the furnace.

The furnace controls are designed so that any rate of heating up to about 12° per minute can be obtained in the range from room temperature to 1,000° C, or any temperature in this range can be maintained indefinitely within 1° C after equilibrium has been reached. However, a selected temperature can be attained only within 3 to 5° C, because the furnace tends to overshoot the selected temperature during initial heating. The essential mechanism of the controls comprises (1) a wire passing vertically between the heating element and the silica glass shell of the heating chamber; changes in the length of the wire with variation of temperature in the furnace actuate (2) a lever, on the outer end of which is mounted both a flexible fillet of metal grounded to the frame of the balance and a metal rod insulated from the metal fillet and connected to the secondary of a 110 - 8-volt transformer. Unless held apart the fillet and the rod are in contact, causing current to flow to the furnace windings. The end of the fillet rides against a strip of cardboard or similar material mounted on (3) a drum driven by a spring chronometer mechanism and rotating either one or two turns in 24 hours, depending upon the setting selected. The strip or guide of cardboard or similar material mounted on the drum is so placed as to yield the desired cycle of temperature rise or fall when the end of the fillet is in contact with it.

As the temperature of the furnace rises, the wire expands, (1) actuating the lever (2) and raising the flexible fillet against the guide on the drum. This contact flexes the fillet and separates it from contact with the rod. Current flowing to a solenoid thus is interrupted, a mercury switch is caused to open, and current to the furnace is cut off. As the temperature-control drum rotates, pressure of the flexible fillet on the guide is reduced, contact of the fillet and rod is resumed, current flows to the solenoid, the switch is closed, and current flows to the furnace to resume heating. Cooling of the furnace produces the same action as does rotation of the temperature-control drum.

The Recording System

The recording system is photographic and is designed to record instantaneously and continuously deflection of the balance beam incidental to changes of weight of the sample during the heating cycle. An 8-volt incandescent bulb yielding approximately a point source is situated 110 cm from the mirror mounted on the end of the beam of the balance and 5.5 cm laterally from a projection of the beam. Light from the bulb passes through a pinhole 0.1 to 0.2 mm in diameter and a collimating lens system into a housing into which the beam of the balance projects. The light is reflected back from the mirror to sensitized paper or film mounted on a drum set on a vertical axis and actuated by a synchronous, electric motor. The cylinder is 9½ inches long and 3⅝ inches in diameter. The rate of rotation can be set at one turn in 2.5 hours or one turn in 20 hours (with 60-cycle current). The recording film or paper is 9½ inches by 11⅝ inches and is wrapped tightly around the drum. We have had success with Ansco Reprolith Ortho film, Emulsion No. C847-2, a product characterized by small and uniform shrinkage with processing and aging.

The record is calibrated by loading a platform on the sample-supporting system with weights of 50, 100, 150 mg, and so forth, and later measuring the shift in position of the trace on the film.

Marks indicating the position of the trace at selected temperatures, usually at multiples of 100° C, are imposed on the film by closing an electrical contact which activates a solenoid controlling a slit in front of the light source. Opening of the slit flashes an additional beam of greater dimensions on the film. Temperature of the furnace is obtained as required by observation of a previously calibrated potentiometer connected to the thermocouple located in the furnace near the specimen under test.

CONTROL OF ERRORS

General Statement

Several phenomena associated with the thermal balance analysis and several problems arising in measuring the record produced must be evaluated and controlled in order that satisfactory results can be obtained.

Selection of Recording Media

The manufacturers of the balance recommend sensitized paper to record the trace of light reflected from the mirror mounted on the beam of the balance. However, sensitized photographic papers we have tested do not shrink uniformly during processing. As a result, records on paper warp and distort excessively. Furthermore, sensitized paper is subject to considerable shrinkage and expansion as a result of changes in humidity.

Ansco Reprolith Ortho film produces an excellent record, and processing does not cause significant shrinkage in any direction. Age produces small shrinkage (0.07 to 0.08 mm per 10 cm during the first several months) which is uniform in all directions, within the limit of our methods of measurement.

Reading the Record

By using a combination of a scale graduated in centimeters and a Bausch and Lomb spectrum plate magnifier graduated in 0.1 mm, the record can be read to ± 0.1 mm. This is verified by repeated readings on the same record. The procedure used in measuring the record in this study is illustrated in Figure 2.

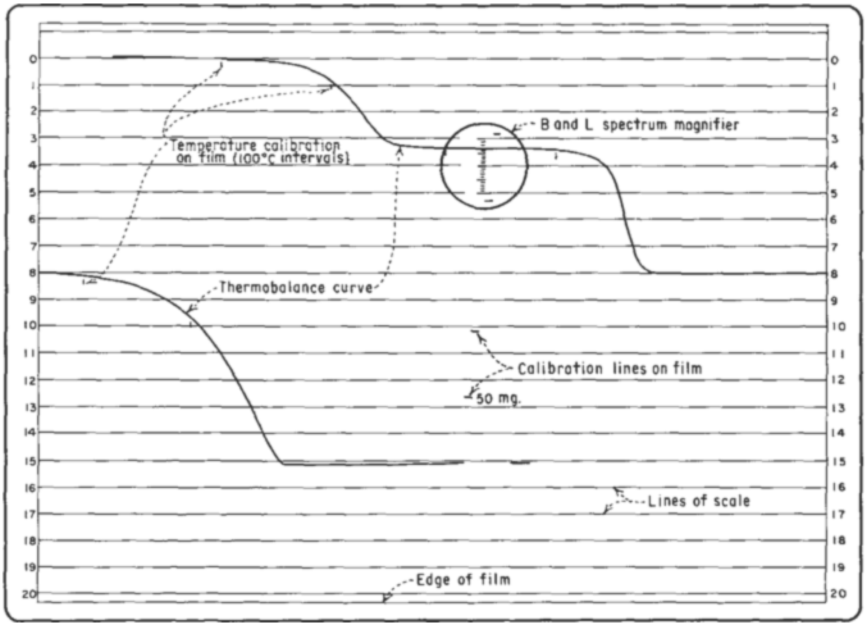

FIGURE 2. — Arrangement for reading the record produced by the thermal balance.

For a 50-mm (approximately 100 mg) deflection (a common deflection obtained in analysis of clay and clay-like minerals), this range of 0.2 mm represents approximately 0.4 mg or four parts per 1,000 variation in a group of readings repeated on the same record. This error is insignificant for most purposes.

Calibration of the Record

Owing to the geometry of the recording mechanism, careful calibration of the record is necessary. Near the top and bottom of the record (*i.e.*, where the beam of the balance departs the most from the horizontal), the light spot traverses a longer film distance than it does near the center of the film for the same angular deflection of the beam. However, inasmuch as the light source is 2.5 cm below the center of the film, the greatest error occurs in readings taken near the top of the film, unless duly corrected. This is illustrated by measurement of deflections produced by addition of weights of 50 mg intervals.

Interval (mg)	Run No. 70 Deflection (mm)	Run No. 73 Deflection (mm)
0-50	24.50 (bottom)	[1] 24.55
50-100	24.50	24.65
100-150	24.60	24.65
150-200	24.60	24.60
200-250	24.60	24.70
250-300	24.70 (top)	[2] 24.80

[1] 1 mm on the record is equivalent to a change in weight of 2.0366 mg.
[2] 1 mm on the record is equivalent to a change in weight of 2.0161 mg.

Run 73 is an analysis of calcium oxalate (0.5000 g sample) in which the weight loss caused a deflection of 150.60 mm. Selecting a calibration factor of 2.0366 mg/mm yields an apparent weight loss of 62.436 percent, whereas the factor 2.0161 yields an apparent weight loss of 61.818 percent.

The most reliable method of calibrating the record seems to be the recording of the deflections produced by successive additions of 50 mg weights at the end of an analysis until the deflection of the beam due to loss in weight of the sample has been approximately counterbalanced. Those 50 mg steps which correspond to the break in question on the record are used in measuring and correcting the weight losses.

Other less accurate methods include (1) recording one 50 or 100 mg deflection anywhere on the record and then using the resulting value for all parts of the curve, or (2) approximately counteracting the full beam deflection occurring during the run and taking the total weight required to produce the counteraction to obtain the calibration of mg/mm of deflection on the record.

Appreciable variation in the calibration of the records occurs over a period of time. No explanation for this can be offered at present. However, if each record is carefully calibrated as described in the second paragraph above, results of the analyses show good agreement. The extreme values for this factor obtained from some 60 records are 1.995 and 2.088 mg/mm.

Errors Due to Buoyancy Effects

Errors arising from change in buoyancy depend on two factors, namely, (1) the apparent loss in weight of the sample because of decrease of density of the atmosphere in the furnace with heating, and (2) convection currents resulting from unequal temperature of the air in and surrounding the furnace. When the top of the furnace is closed, as it is for ordinary determinations, these two effects are additive.

Calculation shows that at 1,000° C the buoyancy effect amounts to 0.000713 g/cc of sample, container, and silica supporting rod. For a 1.5 g sample of aluminum oxide (Al_2O_3), that volume is 3.435 cc, and the calculated buoyancy effect requires a correction of 0.00245 g in the weight loss-time curve. This correction is added to the recorded weight loss.

A run in the furnace with inert calcined aluminum oxide was made to determine empirically the combined effects of buoyancy and convection currents. The first complete revolution of the recording drum was made with the furnace at room temperature; the second revolution was made with the furnace operating normally at a heating rate of 5° C/min. The buoyancy correction at 1,000° C was found to be 0.00572 g for a 1.5 g sample. In other words, the inert sample appeared to have gained 0.00572 g. This indicates a correction of $0.00572 - 0.00245 = 0.00327$ g/1.5 g sample for the combined other effects, the most important of which are convection currents.

Several experiments with 1.5000 g samples and one with a 2.2500 g sample showed the same general characteristics for the correction curve and very little variation in the correction curve with change in sample weight. Hence, it was possible to prepare an average correction curve for these combined effects (Fig. 3). This curve shows a rather large correction at the beginning and end of the run and less correction at intermediate temperatures.

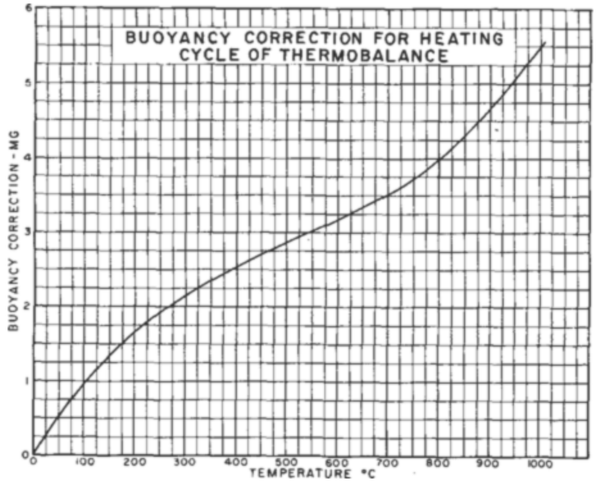

FIGURE 3. — Buoyancy correction for heating cycle of the thermal balance.

The buoyancy correction is significant if the total weight loss is low. This can be demonstrated by the following example: Assume a 1.0000 g sample showing a deflection corresponding to a weight loss of 50 mg (approximately 2.5 cm) in the recorded curve. The indicated loss then is $\frac{0.0500 \times 100}{1.0000} = 5.00$ percent without correction and $\frac{0.0555 \times 100}{1.0000} = 5.55$ percent with correction for the buoyancy effect, or a difference of approximately 0.6 percentile.

Errors Resulting from Thermal Expansion of the Record

Measurements made on processed Ansco Reprolith Ortho film at 24.5° C and at 35° C yielded results that were the same within the experimental error of the method used (± 0.1 mm). The thermal coefficient of expansion of this film thus is negligible with reasonable change of temperature between calibration and measurement of the record.

Errors in Calibration of the Furnace Temperature

When the furnace is operating on a predetermined heating cycle, it should be possible to attach an automatic mechanical device to flash the light at time intervals equivalent to a selected temperature interval, since both the drum controlling the temperature rise and the cylinder recording weight loss are operated by time-measuring devices. A relationship between the time-loss and the temperature-loss curves could then be established to correct the time-loss curve into a temperature-loss curve. This procedure is suggested by Duval (1953, p. 24-25).

However, comparison of the time intervals required for carefully measured 100° C intervals among numerous temperature-loss records demonstrates that this procedure is not feasible, since the time intervals required for the same intervals of temperature rise (e.g., 500° to 600° C or 800° to 900° C) vary appreciably from one record to another. Measurements of the 300-400° C interval on 12 succeeding records show a variation ranging between 41 mm and 43 mm travel of the records. This would amount to a variation of approximately 5° C or ± 2.5° C if we assume 42 mm to be the average travel for this 100° interval. The above-cited example does not represent the maximum variation observed.

It is therefore apparent that automatic recording of temperatures must be based upon a system controlled by the temperature of the furnace in the vicinity of the sample. Such a system is now being developed in our laboratories.

Checking the Thermal Balance Against the Analytical Balance

Both the analytical and thermal balance may yield errors due to improper adjustment of the mechanism. These are fundamental and will not be compared here. Other errors arise from change in weight of the sample after the weighing on the analytical balance and before the start of the thermal-balance run, and after the end of the thermal-balance run and before the final weighing on the analytical balance.

If substances, such as CaO, that react with the constituents of the atmosphere are the end product of the thermal treatment, less weight loss is indicated by the analytical balance than by the thermal balance. Differences in handling such samples between the end of the thermal-balance run and weighing on the analytical balance are definitely apparent in the final results. Rapid cooling of the end product and rapid weighing minimize this error. If the end products are fairly stable and reasonable care is exercised, the agreement between the two balances is usually within 0.1 or 0.2 percent. For example, in 14 thermal analyses of a montmorillonite-type clay, the following divergence in results was found:

Divergence between thermal balance and analytical balance	*Number of determinations*
0.03 percent or less	8 out of 14
.05 percent or less	11 out of 14
.10 percent or less	12 out of 14
.17 percent or less	14 out of 14

REPRODUCIBILITY

Reproducibility and accuracy of the thermal balance is good. For pure calcite the maximum deviation found between the results of three analyses was 0.19 percent (Table 1). The maximum deviation from both the calculated average and the theoretical weight loss due to evolution of CO_2 was 0.10 percent.

TABLE 1. — REPRODUCIBILITY OF RESULTS OBTAINED ON CALCITE ($CaCO_3$) WITH THE THERMAL BALANCE

	Loss (percent)[1] as determined by			
	the thermal balance			
Thermal Balance Run No.	Calculation based on first reading	Calculation based on second reading	Difference due to reading errors	the analytical balance
1	43.98	44.05	0.05	43.50
2	43.90	43.88	.02	43.61
3	44.02	44.07	.05	43.55
Average	43.967	44.00	.04	43.553

[1] Theoretical CO_2 content is 43.97 percent.

The maximum difference due to error in reading the record for individual analyses is 0.07 percent, so that the reproducibility and accuracy on the basis of these analyses are very close to the experimental error of the method.

The maximum difference obtained on the analytical balance between the three determinations was 0.11 percent.

Similar studies with CP grade calcium oxalate ($CaC_2O_4 \cdot H_2O$), dried at 95° C before analysis, gave a maximum difference of 0.40 percent for the water content and 0.25 percent and 0.22 percent for the CO and CO_2 content (Table 2). The maximum difference for the total weight loss was 0.16 percent with the thermal balance and 0.34 percent with the analytical balance. The maximum error involved in rereading and recalculating the records was 0.14 percent. Somewhat larger discrepancies were found

TABLE 2. — REPRODUCIBILITY OF RESULTS OBTAINED ON CALCIUM OXALATE WITH THE THERMAL BALANCE

	Loss of constituents (percent)															Total loss (percent) by thermal balance			
	Based on original sample weight									Based on dehydrated sample weight									
	H_2O			CO			CO_2			CO			CO_2						
Thermal Balance Run No.	First reading	Second reading	Difference	First reading	Second reading	Difference	First reading	Second reading	Difference	First reading	Second reading	Difference	First reading	Second reading	Difference	First reading	Second reading	Difference	Analytical balance
1	13.73	13.71	0.02	19.00	19.00	0.00	29.49	29.38	0.11	22.03	22.01	0.02	34.20	34.06	0.14	62.22	62.09	0.13	62.02
2	13.33	13.32	.01	19.16	19.09	.07	29.61	29.60	.01	21.99	22.02	.03	34.15	34.15	.00	62.10	62.01	.09	61.90
3	13.45	13.36	.09	19.19	19.25	.06	29.59	29.57	.02	27.19	22.23	.04	34.18	34.13	.05	62.07	62.17	.10	61.68
Maximum difference	0.40	0.39	—	0.19	0.25	—	0.12	0.22	—	0.20	0.22	—	0.05	0.09	—	0.15	0.16	—	0.34
Theoretical	12.33			19.17			30.12			21.87			34.37						

between the experimental results and the calculated theoretical values than were found for calcite. Supplementary studies have revealed that the water content of calcium oxalate changes appreciably between room temperature and 95° C.

SELECTION OF THE END POINT OF THERMAL REACTIONS

If the end of a deflection in the trace of the weight-loss temperature curve is horizontal, the temperature at the end of the reaction, under conditions of the experiment, can be established readily. If the curvilinear trace produced by a reaction is interrupted by a second deflection marking the initiation of another reaction, the end point of the first reaction cannot be established accurately.

If a deflection terminates in a straight sloping trace which is in turn terminated by a second deflection, best results are obtained in calculating weight loss if the end point of the first reaction is taken where the negative rotation of the tangent begins.

Selection of an end point for thermal reactions of clay and clay-like minerals from experimental data for individual specimens is necessary for satisfactory analysis. However, several workers have selected certain stipulated temperatures as end points, such as 300° C for the temperature at which adsorbed water has been lost from all montmorillonite-type minerals. Selection of the end point for this reaction establishes the base weight for the sample used, and hence determines the results of the thermal analysis. The thermal balance demonstrates that adsorbed water is lost completely at temperatures ranging from 330° to 560° C for minerals of the montmorillonite group, when the temperature of the sample is raised at the rate of 5° C per minute.

THERMAL ANALYSIS OF HYDROXIDES AND HYDROUS OXIDES

Diaspore (Curve 1, Figures 4 and 5)

Although natural, the diaspore is fairly pure; 13.7 percent by weight of water is given off, using 300° C as the base temperature, compared with the theoretical water content of 15.0 percent. Very small amounts of adsorbed water are lost below 300° C. An inflection point at 300° C approximates the beginning of the loss of hydroxyl water. This reaction is almost complete by 700° C, although a slight weight loss continues through 850° C.

According to the differential thermal curve, the dehydration begins at 425° C, and the reaction is essentially complete by 700° C. A small exothermic reaction takes place at 860° C to 940° C. X-ray diffraction analysis proves corundum is formed at 700° C and that this compound exists after heating to 1,000° C. Both the dehydration curve and the differential thermal curve indicate that the structural water of diaspore is liberated at only one energy level. Both curves are perfectly symmetrical.

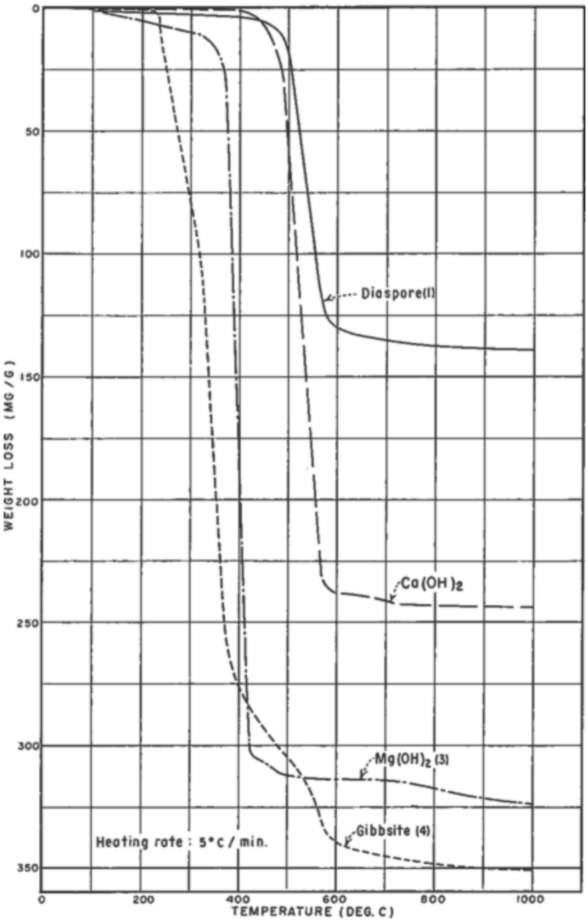

FIGURE 4. — Thermal balance (dehydration) curves for hydroxides and hydrated oxides.

Curve 1. Diaspore, Rosebud, Missouri
Curve 2. Calcium hydroxide, laboratory prepared
Curve 3. Magnesium hydroxide, laboratory prepared
Curve 4. Gibbsite, Baker's C.P. grade

$Ca(OH)_2$ (Curve 2, Figures 4 and 5)

The sample of calcium hydroxide was prepared in the laboratory by igniting CP grade calcium carbonate to calcium oxide, slaking the calcium oxide in distilled water and drying the hydrated product over soda-lime. Small amounts of adsorbed water are lost below 300° C, the base temperature. At 390° C, pronounced water loss begins. This reaction continues up to about 630° C. A second loss of water begins at about 630° C and is

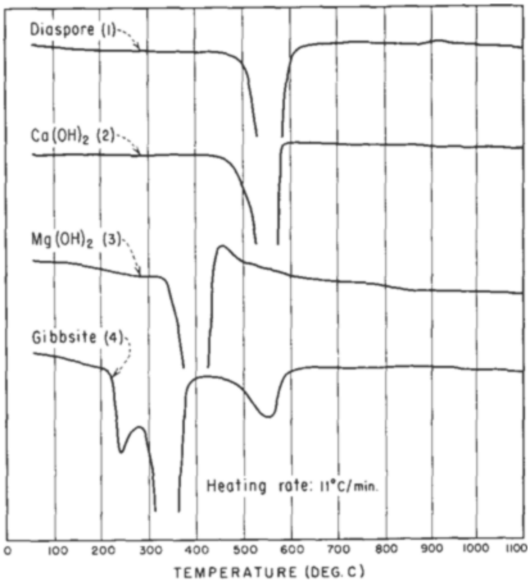

FIGURE 5. — Differential thermal curves for hydroxides and hydrated oxides.
Curve 1. Diaspore, Rosebud, Missouri
Curve 2. Calcium hydroxide, laboratory prepared
Curve 3. Magnesium hydroxide, laboratory prepared
Curve 4. Gibbsite, Baker's C.P. grade

virtually complete by 750° C. According to differential thermal analysis, dehydration begins at 410° C, and the reaction is complete by 600° C. The amount of hydroxyl water evolved was determined to be 24.4 percent, compared with 24.3 percent indicated by the theoretical formula.

$Mg(OH)_2$ (Curve 3, Figures 4 and 5)

The sample of magnesium hydroxide was prepared in the laboratory by dissolving CP grade magnesium chloride in distilled water, precipitating $Mg(OH)_2$ with ammonium hydroxide, filtering and washing with distilled water, then drying the magnesium hydroxide over soda-lime. Small amounts of water are lost below the base temperature, 260° C. Both the differential thermal and the thermal balance curves indicate that magnesium hydroxide begins to lose hydroxyl water at or slightly above 135° C. A distinct inflection occurs in the thermal balance curve at 425° C, after loss of the bulk of the hydroxyl water. The thermal balance curve indicates that the decomposition of magnesium hydroxide to magnesium oxide is essentially complete by 850° C. This is the temperature at which the differential thermal curve returns to the base line after a mild exothermic reaction which attains a maximum at 460° C. The thermal balance analysis indicates that carbonate is insufficient in amount to account for the reaction beginning at 690° C.

Gibbsite (Curve 4, Figures 4 and 5)

The sample of gibbsite analyzed is CP grade $Al_2O_3 \cdot 3H_2O$ which is identical crystallographically with natural gibbsite according x-ray diffraction and differential thermal analysis. The differential thermal and thermal balance curves for gibbsite (natural and synthetic) are unusual in that the curves are made up of three distinct portions. The first dehydration of gibbsite starts at about 210° C and continues through 280° C. The dehydration product of the small amount of gibbsite decomposed in this interval is determined by x-ray diffraction analysis to be boehmite ($Al_2O_3 \cdot H_2O$). The loss of weight during this dehydration amounts to 6.2 percent of the base weight of the sample, taking the base temperature as 100° C. From 280° C to 425° C, a second endothermic reaction occurs, during which the remaining gibbsite dehydrates to a form of boehmite, accompanied by a weight loss of 22.3 percent. After this dehydration reaction, the differential thermal curve returns to base line at 425° C. Immediately thereafter, the third endothermic reaction begins.

Above 425° C, boehmite dehydrates to eta- or gamma-alumina, the reaction being essentially complete at about 900° C. However, the differential thermal curve returns to base line at about 650° C and indicates no reaction from 650° to 1,100° C. The weight loss from 425° to 1,000° C amounts to 6.4 percent.

After heating to 1,000° C, either kappa- or theta-Al_2O_3 is present. No thermal reaction is evident between 700° and 1,000° C on the differential thermal curve.

Not all gibbsites show three main dehydration reactions. Kerr and Kulp (1948, p. 404) found a gibbsite from Brazil to produce three dehydration reactions and one exothermic reaction, which occurred at 980° C. However, they describe a gibbsite from Richmond, Massachusetts, yielding only the first two dehydration reactions and no exothermic reaction. Grim and Rowlands (1942, p. 750) analyzed a gibbsite from Saline County, Arkansas, yielding the second and third dehydration reactions and an exothermic reaction at 950° C. They attributed the third dehydration reaction and exothermic reaction to kaolinite. Spiel (1945, p. 14) reports for gibbsite the second dehydration reaction, a trace of the third reaction, and an exothermic reaction at 980° C. Finally, a differential thermal curve for gibbsite by Beck (1950, p. 519) shows only the second dehydration reaction. A static dehydration curve published by Nutting (1943, p. 204) for synthetic gibbsite is of the same form as Curve 4 (Fig. 4), but the distribution of water loss differs. The first dehydration on Nutting's curve corresponds to the liberation of about 1½ mols of water, the second dehydration to the liberation of 1 mol of water, and the third dehydration to ½ mol of water. Curve 4, however, indicates loss of approximately ½ mol of water during the first dehydration, 2 mols during the second dehydration, and ½ mol of water during the third dehydration.

We conclude from these data that gibbsite typically is a mixture of compounds with the composition $Al_2O_3 \cdot 3H_2O$, and that the relative abundance of these compounds varies with the manner of preparation or the manner of formation of gibbsite under natural conditions. Neither Nutting's nor our data indicate a dehydration reaction of the form

$$\underset{\textit{Gibbsite}}{Al_2O_3 \cdot 3H_2O} \rightarrow \underset{\textit{Boehmite}}{Al_2O_3 \cdot H_2O} + \underset{\textit{Water}}{2H_2O}$$

Rather, boehmite is present in gibbsite which has lost only ½ mol of water per molecule; and a compound whose x-ray diffraction pattern corresponds to that of boehmite is present after the gibbsite has lost 2½ mols of water per molecule. These observations also suggest that the original gibbsite is composed of two or more forms of $Al_2O_3 \cdot 3H_2O$ which dehydrate to boehmite at different temperatures, and that the resulting boehmite exists as polymorphous forms which dehydrate further at somewhat different temperatures.

THERMAL ANALYSIS OF MINERALS OF THE KAOLINITE GROUP

Dickite (Curve 5, Figures 6 and 7)

Both the differential thermal and the thermal balance curves for dickite indicate that only small amounts of adsorbed water are lost below 300° C (the base temperature) and that the loss of hydroxyl water begins to be noticeable at about 460° C. Dehydration is essentially complete at 960° C. After the large endothermic reaction, the differential thermal analysis curve slopes slightly upward to 960° C, at which temperature a very small endothermic reaction occurs just before the large exothermic reaction.

After heating of the dickite to 1,000° C, mullite, small amounts of gamma-Al_2O_3, and an unidentified mineral were revealed by x-ray diffraction analysis.

The thermal curves for dickite differ from those produced by kaolinite. In the interval from 400° to 800° C, curves produced by kaolinite typically are symmetrical and are always smooth, whereas the curves produced by dickite in this temperature range always contain a straight portion preceding the initiation of the main dehydration. In the differential thermal curve, the straight portion extends from about 550° to 630° C. A similar straight portion is apparent in the original thermal balance curve, but this portion of the curve was not reproduced accurately in the figure.

Serpentine (Antigorite) (Curve 6, Figures 6 and 7)

Small amounts of adsorbed water are lost from antigorite below 300° C. An inflection occurs on the thermal balance curve at 310° C, which is

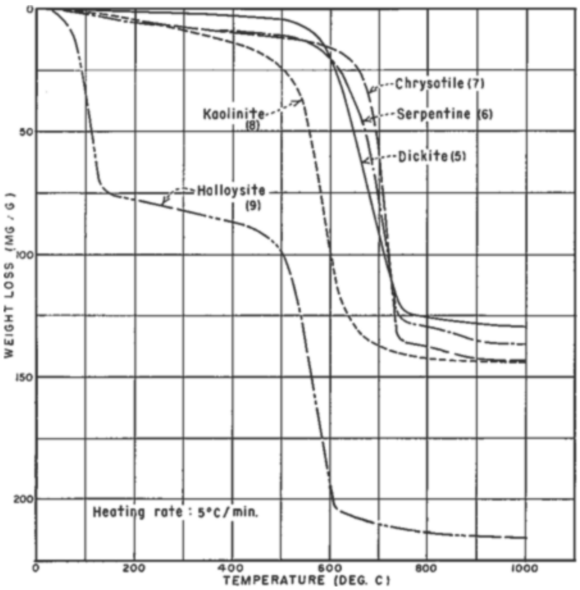

FIGURE 6. — Thermal balance (dehydration) curves for minerals of the kaolinite group.

Curve 5. Dickite, Red Mountain, Colorado
Curve 6. Serpentine (antigorite), Warren County, New York
Curve 7. Chrysotile, Quebec, Canada
Curve 8. Kaolinite, Macon, Georgia
Curve 9. Halloysite, Eureka, Utah

taken as the base temperature. At higher temperatures the mineral loses hydroxyl water. The differential thermal analysis curve indicates this reaction begins at about 500° C. Water loss is rapid from 600° C through 740° C. A straight portion occurs between 610° and 660° C in both curves, and is similar to that at the beginning of the dickite dehydration. The first reaction is complete by 780° C. At this temperature a second loss of water begins and is completed by 940° C. This loss of structural water occurs in a temperature range in which the differential thermal curve indicates an exothermic reaction. Following the exothermic reaction, a small endothermic reaction centers at 870° C. This corresponds to a sloping part of the thermal balance curve. Above 930° C, the differential thermal curve returns to base line. X-ray diffraction analysis indicates that forsterite is the only mineral present after heating of antigorite to 1,000° C.

Chrysotile (Curve 7, Figures 6 and 7)

A small amount of adsorbed water is released from chrysotile below 340° C, but loss of hydroxyl water begins slowly at 340° C, according to the thermal balance. This is established as the base temperature. At low

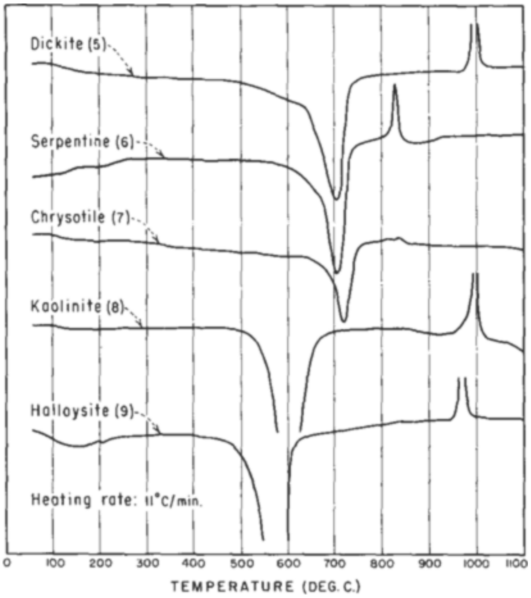

FIGURE 7. — Differential thermal curves for minerals of the kaolinite group.
Curve 5. Dickite, Red Mountain, Colorado
Curve 6. Serpentine (antigorite), Warren County, New York
Curve 7. Chrysotile, Quebec, Canada
Curve 8. Kaolinite, Macon, Georgia
Curve 9. Halloysite, Eureka, Utah

temperatures the differential thermal curve shows no reaction, but at 330° C, the curve begins to slope noticeably. At 640° C, rapid loss of water begins. This loss of water continues to about 780° C, where a second dehydration begins. A short straight trace similar to that developed by dickite and serpentine (antigorite) is produced between 640° and 670° C on the thermal balance curve. Only a suggestion of this straight section is apparent in the differential thermal curve.

A second increment of water is evolved from 780° C through 950° C. Only a suggestion of water loss is apparent on the differential thermal curve at 860° C. A small exothermic reaction beginning at 840° C is accompanied by a small water loss as indicated on the thermal balance curve. X-ray diffraction reveals only forsterite after heating to 1,000° C.

Kaolinite (Curve 8, Figures 6 and 7)

Both the thermal balance and differential thermal curves are symmetrical in the range of loss of structural (hydroxyl) water. Only small amounts of water are liberated below 265° C. An inflection point occurs at 265° C (the base temperature) on the thermal balance curve, but loss of water is not rapid until about 460° C.

After the large endothermic reaction, the differential thermal curve returns to base line at about 800° C. A slight endothermic reaction occurs between 840° and 920° C, probably being due in part to absorption of energy initiating crystallization and in part to evolution of residual water. Only 0.05 percent of water is lost from 840° to 920° C.

Crystallization of gamma-alumina is indicated by the exothermic reaction at 950° to 1,010° C. Gamma-Al_2O_3 is the only compound present after heating to 1,000° C, according to x-ray diffraction analysis.

Halloysite (Curve 9, Figures 6 and 7)

According to both types of thermal curves, halloysite loses adsorbed water from slightly above room temperature to 320° C. The thermal balance curve indicates that hydroxyl water begins to evolve at 320° C, which is taken as the base temperature.

Both curves indicate that loss of hydroxyl water is rapid above about 450° C. The loss is evident to 900° C on the differential thermal curve and to about 960° C on the thermal balance curve. The dehydration curve for halloysite, in contrast to that of kaolinite, is asymmetrical. A sharp break occurs in the dehydration curve at about 610° C; this corresponds to the very steep portion of the differential thermal curve at about 600° C. The differential thermal curve shows the familiar exothermic reaction at 945° to 1,000° C, representing crystallization of gamma-Al_2O_3. Water loss totals 0.01 percent from 945° to 1,000° C.

THERMAL ANALYSIS OF MICAS AND RELATED HYDROUS SILICATES

Biotite (Curve 10, Figures 8 and 9)

The differential curve for the sample of biotite tested shows no indication of a thermal reaction from room temperature to 1,100° C. Only a small amount of water is liberated, and this release occurs uniformly over the whole range from 100° C (the base temperature) to 1,000° C. No change in the structure of biotite was observed by x-ray diffraction analysis following thermal treatment to 1,100° C.

Lepidolite (Curve 11, Figures 8 and 9)

The thermal balance curve shows only a slight loss of water up to 800° C. Loss of structural water begins at 800° C and continues through 1,000° C; the base temperature is 100° C. The differential thermal curve similarly suggests no loss of water up to 790° C. At higher temperatures, the endothermic reaction is rapid and is completed by 950° C, at which temperature the differential thermal curve returns to base line. Apparently, fluorine is not liberated during this dehydration reaction.

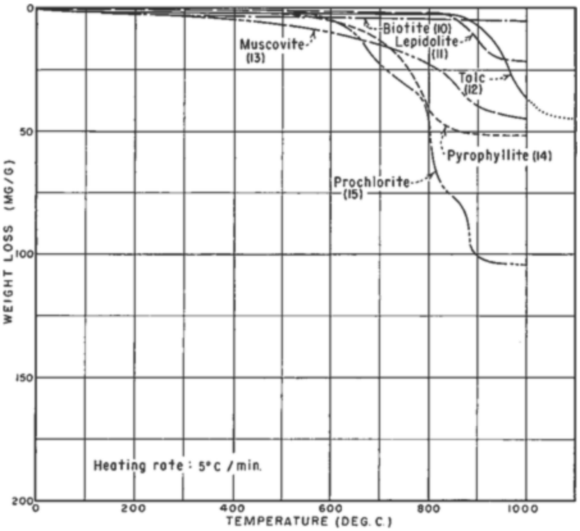

FIGURE 8.— Thermal balance (dehydration) curves for micas and micaceous minerals.
Curve 10. Biotite, Bancroft, Ontario, Canada
Curve 11. Lepidolite, Oxford County, Maine
Curve 12. Talc, Providence, Rhode Island
Curve 13. Muscovite, source unknown
Curve 14. Pyrophyllite, Staley, North Carolina
Curve 15. Prochlorite, Chester, Vermont

Talc (Curve 12, Figures 8 and 9)

The thermal curves for talc indicate only a slight loss of water up to 850° C. The base temperature is 100° C. Above 850° C, loss of hydroxyl water begins and an endothermic reaction is indicated by the differential thermal curve. According to differential thermal analysis, the endothermic reaction is complete at about 1,035° C; however, the thermal balance curve indicates that talc is still dehydrating rapidly at 1,000° C. The dotted line (Fig. 9) indicates loss of weight occurring while the furnace is held at approximately 1,000° C for 1 hour. According to x-ray diffraction, the original lattice structure of talc still remains after heating of the sample to 1,000° C. Only a slight amount of distortion and line shifting in the patterns results from the heating.

Muscovite (Curve 13, Figures 8 and 9)

The sample of muscovite begins to lose small amounts of water above 100° C, which is taken as the base temperature. Above 700° C the loss of water is rapid, and the reaction is nearly but not quite complete at 1,000° C. The differential thermal curve reveals no loss of water from room temperature to about 700° C. At this temperature, the curve deviates from the base line and continues downward through 1,100° C.

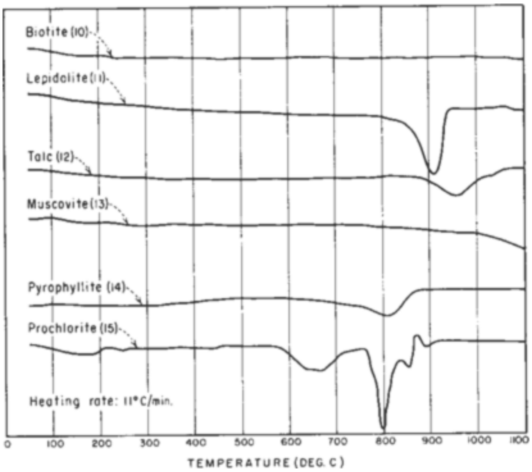

FIGURE 9. — Differential thermal curves for micas and micaceous minerals.
Curve 10. Biotite, Bancroft, Ontario, Canada
Curve 11. Lepidolite, Oxford County, Maine
Curve 12. Talc, Providence, Rhode Island
Curve 13. Muscovite, source unknown
Curve 14. Pyrophyllite, Staley, North Carolina
Curve 15. Prochlorite, Chester, Vermont

Pyrophyllite (Curve 14, Figures 8 and 9)

Pyrophyllite loses minute amounts of adsorbed water from 25° C through 470° C. The base temperature is established at 100° C. Above 470° C, loss of hydroxyl water begins and is virtually complete by 900° C. The differential thermal curve indicates no reaction below 600° C. An endothermic reaction begins at 600° C and is complete at 890° C. No reactions occur above 890° C.

Line shifting and distortion are slight in the x-ray diffraction pattern of the pyrophyllite, as a result of heating to 1,000° C.

Prochlorite (Curve 15, Figures 8 and 9)

According to the thermal balance curve, prochlorite loses virtually no weight between 25° and 500° C. The base temperature is 100° C. From 510° to 760° C, the first portion of structural water is lost. This corresponds to the endothermic reaction indicated by the differential thermal curve between 580° and 760° C. From 760° to 855° C, the second portion of hydroxyl water is evolved. This corresponds to the endothermic reaction extending from 760° to 830° C. A third and final loss occurs between 855° and 1,000° C. The differential thermal curve reveals a third small endothermic reaction between 830° and 860° C.

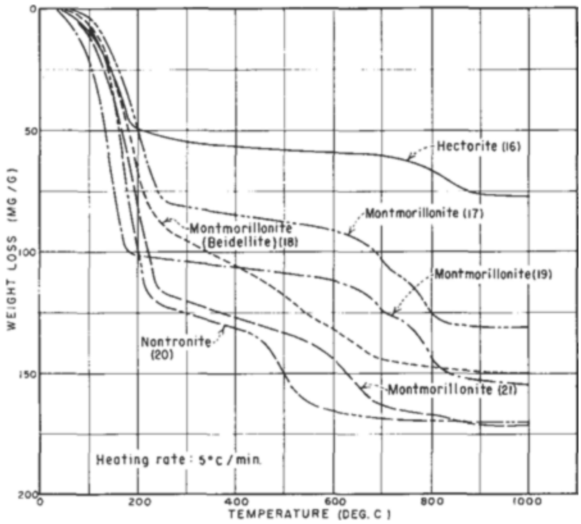

FIGURE 10. — Thermal balance (dehydration) curves for minerals of the montmorillonite group.
Curve 16. Hectorite, Hector, California
Curve 17. Montmorillonite, Upton, Wyoming (purified and changed to Ca^{2+} form in the laboratory)
Curve 18. Montmorillonite (beidellite), Anderson Ranch Dam site, Idaho
Curve 19. Montmorillonite, Belle Fourche, South Dakota
Curve 20. Nontronite, Manito, Washington
Curve 21. Montmorillonite, Otay, California

While dehydration is progressing, an exothermic reaction occurs at about 870° C and is followed by a slight endothermic reaction from 890° to 920° C. Above this temperature no further reactions are indicated.

The final reaction product at 1,000° C is olivine, which crystallized at about 870° C.

THERMAL ANALYSIS OF MINERALS OF THE MONTMORILLONITE GROUP

Hectorite (Curve 16, Figures 10 and 11)

Both the thermal balance and differential thermal curves show loss of adsorbed water between 100° and 200° C. The differential thermal curve also shows a small endothermic reaction between 200° and 300° C. According to the thermal balance, loss of adsorbed water continues to 560° C, the base temperature. A second slight endothermic reaction occurs from 510° to 650° C, and a third endothermic reaction takes place between 750° and 910° C. This reaction corresponds to the loss of weight shown on the dehydration curve from 560° to 1,000° C. An endothermic reaction is indicated in the range from 1,040° to 1,100° C.

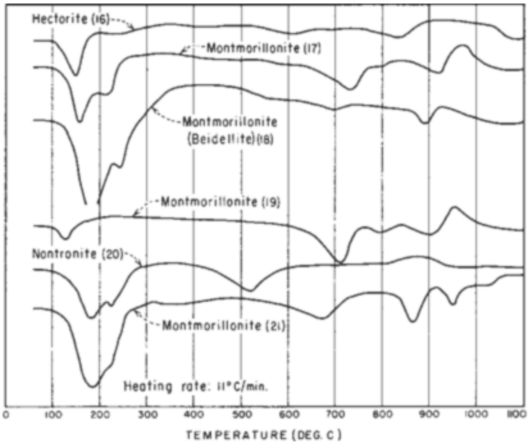

FIGURE 11. — Differential thermal curves for minerals of the montmorillonite group.
Curve 16. Hectorite, Hector, California
Curve 17. Montmorillonite, Upton, Wyoming (purified and changed to Ca^{2+} form in the laboratory)
Curve 18. Montmorillonite (beidellite), Anderson Ranch Dam site, Idaho
Curve 19. Montmorillonite, Belle Fourche, South Dakota
Curve 20. Nontronite, Manito, Washington
Curve 21. Montmorillonite, Otay, California

Montmorillonite (Curve 17, Figures 10 and 11)

The differential thermal curve shows a pronounced endothermic reaction from 90° to about 200° C. This is followed by another endothermic reaction from 200° to 260° C. The first endotherm probably represents loss of interlayer water, whereas the second represents loss of water associated with the exchangeable Ca^{2+}. The thermal balance curve demonstrates that adsorbed water is evolved in this temperature range. At 190° C, the slope of the curve decreases slightly, indicating release of a different phase. The differential thermal curve returns to base line at 330° C.

A definite inflection point occurs on the thermal balance curve at 480° C, marking approximately the beginning of loss of hydroxyl units from the structure. The loss of the first portion of the hydroxyl water continues up to 740° C, and totals 3.0 percent. This is the base temperature. The equivalent endothermic reaction appears to begin at about 550° C and continues through 770° C. The second loss of hydroxyl water (1.9 percent) begins at 740° C and continues through 920° C, after which only 0.05 percent of water is lost. The second loss of hydroxyl water corresponds to the small endothermic reaction between 780° and 810° C. The endothermic reaction at 850° to 930° C is much too large to correlate specifically with the very small amount of water evolved from 850° to 930° C, namely 0.07 percent. The exothermic reaction above 930° C is accompanied by loss of negligible amounts of water.

Montmorillonite (Beidellite) (Curve 18, Figures 10 and 11)

Adsorbed water is released at temperatures up to 390° C (the base temperature), and an endothermic reaction takes place between 100° and 450° C. A subordinate endothermic reaction occurs at 225° to 250° C, but no inflection is evident in the thermal balance curve.

At 390° C, structural (hydroxyl) water begins to evolve. The first structural water is given off between 390° and 595° C. The differential thermal curve trends downwardly from 450° C, attains a maximum at 550° C, and levels off at about 620° C.

A second portion of structural water is lost from 595° C to 950° C. The endotherm at 700° C (peak temperature) corresponds to the break in the dehydration curve at 700° C. The endotherm and exotherm at 895° and 920° C (peak temperatures), respectively, have no counterpart on the thermal balance curve. This endothermic-exothermic reaction begins at 850° C and ends at about 1,000° C.

Montmorillonite (Curve 19, Figures 10 and 11)

The thermal balance and differential thermal curves both indicate loss of adsorbed water between 25° and 220° C. The differential thermal curve suggests that the reaction is complete at 220° C, whereas the thermal balance curve indicates that the loss continues to 405° C (the base temperature). At 405° C, structural (hydroxyl) water begins to evolve. The first loss is complete by 725° C. This water loss, which amounts to 2.2 percent, corresponds to the endotherm between 500° to 750° C.

The second loss of hydroxyl water occurs between 725° C and 870° C and is analogous to the endotherm on the differential thermal curve from 750° to 850° C. The loss of hydroxyl water amounts to 3.0 percent.

A third portion of structural water (0.34 percent) is lost between 870° and 1,000° C, the reaction being essentially complete by 970° C. This loss of water is approximately contemporaneous with the endotherm at 850° to 920° C, and the following exothermic reaction from 920° to 1,000° C. However, the endotherm from 850° to 920° C cannot be explained entirely in terms of water loss, inasmuch as this endotherm is larger than the second high-temperature endotherm and yet the third endotherm is associated with 0.34 percent water, whereas the second endotherm is associated with 3.0 percent of water.

Nontronite (Curve 20, Figures 10 and 11)

Nontronite loses adsorbed water from 25° to 300° C, the greatest amount of water being lost from 65° to 225° C. A marked endotherm occurs between 65° and 210° C, and a small endotherm between 210° and 220° C. The thermal balance curve shows no indication of a change in slope from 210° to 220° C, as one would expect from the endothermic reaction. The differential thermal curve returns to base line at about 350° C.

From 330° (the base temperature) to 830° C, structural (hydroxyl) water is evolved, amounting to 4.9 percent. The endotherm on the differential thermal curve starts at 360° C and continues to 780° C. Only a trace of water is lost above 800° C, although a mild exothermic reaction occurs at 810° to 940° C.

Montmorillonite (Curve 21, Figures 10 and 11)

As in the above thermal curves for montmorillonites, the thermal balance and differential thermal curves indicate that adsorbed water is lost from 65° to 465° C. At about 200° C, the slope of the thermal balance curve decreases slightly but abruptly, indicating a change in the association of the water being released. The water lost from 200° to 465° C probably is in part associated with the exchangeable cation. A marked endothermic reaction attains a maximum at 190° C, and a very small endotherm is superimposed at about 225° C. The differential thermal curve returns to base line at about 310° C. A slight endotherm occurs between 315° and 465° C, which is the base temperature established by the thermal balance curve.

Above 465° C, structural water is evolved. The main water loss, which amounts to 4.12 percent, occurs between 590° and 670° C. A broad endotherm is recorded between 490° and 785° C. A second loss of structural water occurs between 785° and 910° C, as is shown by both curves. The endotherm with a peak temperature at 950° C and a rise of the curve at 1,040° C are not associated with weight loss. The weight loss from 410° to 1,000° C amounts to only 0.08 percent.

X-ray diffraction indicates that the principal crystalline compound present after heating to 1,000° C is beta-quartz. According to the microscope, the remainder is glass.

THERMAL ANALYSIS OF MINERALS OF THE HYDROUS MICA GROUP

Celadonite (Curve 22, Figures 12 and 13)

Two endothermic reactions at 145° and 200° C (peak temperatures) are indicated by the differential thermal analysis, but only one stage of dehydration is indicated by the thermal balance curve in the range from 65° to 300° C, although there is a slight decrease in slope at 200° C. At 300° C (the base temperature), celadonite begins to lose structural water. This process continues through 910° C.

Above 300° C, the differential thermal curve is very irregular and corresponds very poorly with the thermal balance curve. Thermal reactions are indicated by the differential thermal curve with maxima at 700°, 950°, and 1,005°, and 1,025° C. These reactions have no counterparts on the thermal balance curve. Evidently water is liberated slowly over long temperature ranges and the energy change involved is not sufficiently intense to be recorded satisfactorily in the differential thermal analysis.

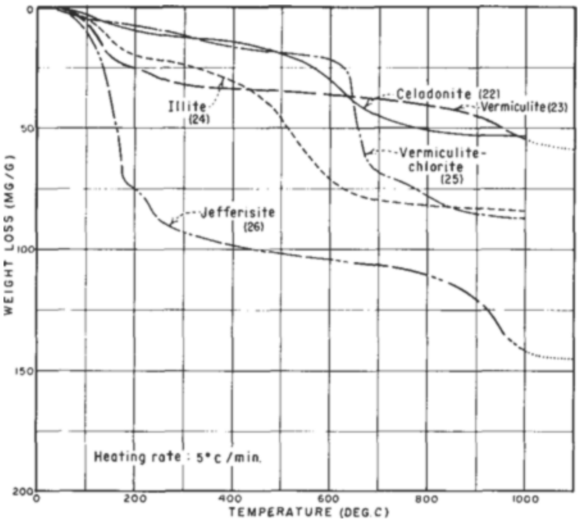

FIGURE 12. — Thermal balance (dehydration) curves for the hydrous micas.
Curve 22. Celadonite, near Twin Falls, Idaho
Curve 23. Vermiculite, source unknown
Curve 24. Illite, Fithian, Illinois
Curve 25. Vermiculite-chlorite, near Salida, Colorado
Curve 26. Jefferisite, Hillside, Colorado

Vermiculite (Curve 23, Figures 12 and 13)

The thermal balance curve shows a loss of adsorbed water from 65° to about 175° C, and a second increment of loss from 175° to 495° C. The second quantity of adsorbed water is evidently associated with the exchangeable cation. In this temperature range, the differential thermal curve shows three endotherms with maxima at 125°, 150°, and 220° C. The reaction at 150° C is not evident on the thermal balance curve.

At 495° C (the base temperature), another inflection in the thermal balance curve marks the beginning of the loss of structural water, which is most rapid between 850° and 1,000° C. The differential thermal curve shows a broad sag from about 500° to 850° C. At 990° to 1,050° C, a small exothermic reaction appears.

The dotted section at the upper end of the thermal balance curve indicates loss of weight while the furnace was held at approximately 1,000° C for 20 minutes.

Illite (Curve 24, Figures 12 and 13)

The thermal balance indicates loss of adsorbed water from 50° to 300° C. An endothermic reaction extends from 50° to 195° C, at which temperature a second very small endotherm begins. The curve returns to the base

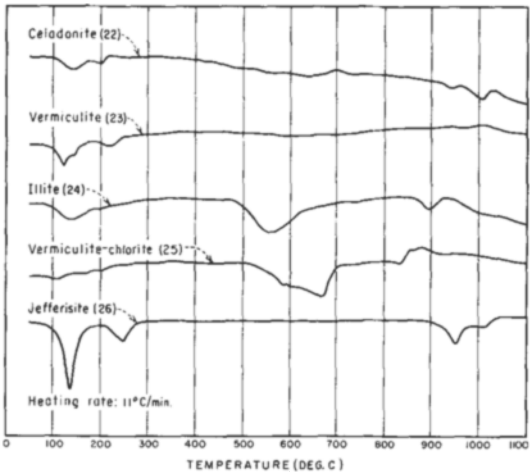

Figure 13. — Differential thermal curves for the hydrous micas.
Curve 22. Celadonite, near Twin Falls, Idaho
Curve 23. Vermiculite, source unknown
Curve 24. Illite, Fithian, Illinois
Curve 25. Vermiculite-chlorite, near Salida, Colorado
Curve 26. Jefferisite, Hillside, Colorado

line at 350° C. On the thermal balance curve, a definite inflection at 300° C (the base temperature) marks the beginning of the evolution of hydroxyl water. A second inflection occurs at 385° C, above which the dehydration is rapid, being essentially complete at 925° C. An endotherm begins at 485° C, attains a maximum at 560° C, and is essentially complete at 740° C.

Another endotherm attains a peak temperature at 900° C and is immediately followed by a small exothermic reaction at 920° C. The thermal balance curve shows a marked decrease in slope at 925° C. The water loss from 900° to 1,000° C amounts to only 0.1 percent, whereas from 850° to 1,000° C only 0.17 percent of water is lost. This amount of water appears to be exceedingly small to be accounted for by the endothermic reaction from 850° to 910° C.

Vermiculite — Chlorite (Curve 25, Figures 12 and 13)

Water is evolved in very small amounts from 25° to 150° C (the base temperature). The total loss in this range is 1.6 percent. The first stage of water loss is probably absorbed and adsorbed water, whereas the later losses are water that is associated with the exchangeable cation. In this temperature range, small endothermic reactions attain maxima at 110°, 165°, and 205° C.

Above 400° C structural water is released, the loss becoming progressively more rapid and attaining a maximum rate at about 650° C. At 700° C, a second loss of structural water begins, being completed at 940°

C. The differential thermal curve shows an endotherm beginning at 500° C, with one peak at 590° C and another at 670° C. A small endotherm begins at 810° C and is followed by double exothermic reactions from 850° to 900° C.

Jefferisite (Curve 26, Figures 12 and 13)

Both thermal curves indicate that absorbed and adsorbed water are lost between 50° and 200° C. This loss is followed by a second dehydration which is rapid through 275° C, but continues to 560° C, the base temperature. A marked endotherm begins just above room temperature, attains a maximum at 135° C, and is completed at 205° C. A second endotherm is indicated between 205° and 295° C. The second loss of adsorbed water is related to water associated with the exchangeable cation.

At 560° C, loss of structural (hydroxyl) water begins. Only very small amounts of water are lost to 850° C, and no indication of this loss is seen on the differential thermal curve. Loss of hydroxyl water is rapid from 850° to 1,000° C, and this loss is coincident with a definite endotherm. A faint endotherm is recorded at 1,000° to 1,035° C.

The dotted line at the end of the thermal balance curve indicates loss of weight while the furnace is held at approximately 1,000° C for 20 minutes.

THERMAL ANALYSIS OF FIBROUS CLAY AND CLAY-LIKE MINERALS

Sepiolite (Curve 27, Figures 14 and 15)

Absorbed and zeolitic water is lost from 50° up to 250° C (the base temperature). Simultaneously, a large endothermic reaction occurs. The thermal curve indicates loss of structural water in steps from 250° to 435° C, 450° to 635° C, and 640° to 1,000° C. The differential thermal curve, however, shows endotherms from 320° to 360° C, from 360° to 450° C, and possibly from 450° to 610° C. An exotherm also occurs from 750° to 850° C, and possibly another between 965° and 1,050° C. X-ray analysis by Migeon (1936, p. 127) indicates that the lattice structure of sepiolite is altered at 350° C; 250° C is selected as the base temperature. At 250° C a definite inflection point is evident on the thermal balance curve. The dotted line at the end of the dehydration curve represents loss of weight while the sample is held at approximately 1,000° C for 15 minutes.

Palygorskite (Curve 28, Figures 14 and 15)

Absorbed and zeolitic water is lost from palygorskite from 65° to 225° C and from 225° to 355° C. The base temperature was set at 225° C, inasmuch as the lattice structure is altered above this temperature. An endotherm extends from 100° to 225° C.

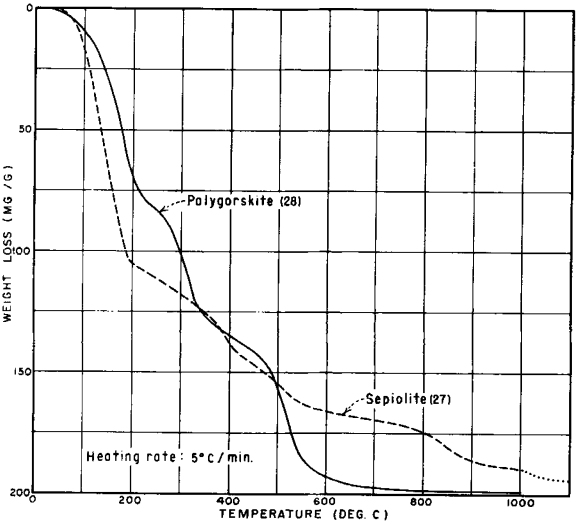

FIGURE 14. — Thermal balance (dehydration) curves for the fibrous clay and clay-like minerals.
Curve 27. Sepiolite, Italian Somaliland, Africa
Curve 28. Palygorskite, Lemesurier Island, Alaska

The first loss of structural (hydroxyl) water occurs between 225° and 355° C, coincident with a marked endotherm. A second loss of structural water takes place between 355° and 800° C, at which temperature the dehydration is virtually complete. Abrupt decrease in slope of the dehydration curve is evident at 535° and 610° C. The differential thermal curve slopes downwardly above 355° C, attains a maximum at 500° C, and returns to a steady line at 630° C. The endotherm at 500° C corresponds to a steep part of the dehydration curve. A small endothermic reaction extends from 900° to 970° C. Neither this reaction nor the exothermic reaction at 970° to 1,025° C is accompanied by loss of water.

CONCLUSIONS

The Chevenard thermal balance is a reliable addition to methods now used in the analysis of clay and clay-like minerals. Dependable results of satisfactory reproducibility can be obtained if techniques described in this paper are used.

Differential thermal analysis and thermal balance analysis yield complementary information on materials, especially in distinguishing and measuring energy changes associated with the taking up or release of substances, in contrast to energy changes associated with crystallographic transformations. Temperature ranges in which rapid dehydration occurs compare closely with temperatures bounding certain endothermic reactions. However, in any one record, the area under the differential

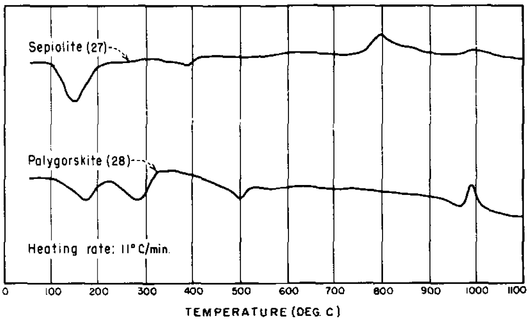

FIGURE 15. — Differential thermal curves for the fibrous clays and claylike minerals.
Curve 27. Sepiolite, Italian Somaliland, Africa
Curve 28. Palygorskite, Lemesurier Island, Alaska

thermal curve is not proportional to the quantity of water evolved since the energy required for its release differs with its mode of combination in the sample. Small and progressive losses of water are indicated poorly or not at all by the differential thermal curve. The transition of loss of water from one mode of combination to loss of water from another mode of combination is recorded better by the differential thermal curve, although the thermal balance usually registers a slight change in slope of the dehydration curve when evolution of the second water phase becomes significant. Endothermic reactions immediately preceding exothermic reactions are likely to mark the beginning of crystallographic changes rather than loss of volatile components.

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