THE AMERICAN MINERALOGIST, VOL. 47, MARCH-APRIL, 1962

A COMPARISON OF TWO METHODS OF DETERMINING HEATS OF REACTION BY DIFFERENTIAL THERMAL ANALYSIS[1]

Boyd G. Ellis and M. M. Mortland, *Department of Soil Science, Michigan State Univ., East Lansing, Mich.*

Abstract

A discussion is presented concerning the factors which affect calibration of a differential thermal analysis apparatus for determination of heats of reaction and the factors affecting the determination of heats of reaction by use of the Clausius-Clapeyron equation. These two methods of determining the heats of reaction are compared by use of magnesite and kaolinite. An average value of 27.6 kilocalories per mole of magnesite decomposed was obtained with 4.7 per cent difference between methods. An average of 156 calories per gram for dehydroxylation of kaolinite was obtained with 1.9 per cent difference between methods of determination.

Introduction

Qualitative differential thermal analysis has been widely used in the study of various minerals. However, quantitative use of the method has been very limited. Various investigators, Norton (1940), Kiyoura and Sata (1950), Murray, *et al.* (1951), and Grimshaw and Roberts (1953), have attempted to utilize differential thermal analysis as a rapid, inexpensive, and accurate method for quantitative determinations of clay minerals. However, considerable differences of opinion have been expressed about the reliability of such use of differential thermal analysis. Speil (1944) found deviations of about 30 per cent in heats of transformation of kaolinite from various locations. Van der Marel (1956) found that the basic limitation in studying clay minerals is in the variation of naturally occurring clay minerals. Inasmuch as the measurements made by differential thermal analysis are of heats of reactions occurring when a sample is heated at a constant rate, several factors inherent with the instrument tend to limit its use as a precise, quantitative instrument. According to Barshad (1952) the peak area is affected by rate of heating, nature of the sample holder, size of the holes in the sample holder, nature of the thermocouple and sensitivity of the galvanometer.

Two methods of measuring ΔH, the change in enthalpy, by use of differential thermal analysis have been suggested in the literature. The dependence of the peak area in differential thermal analysis curves on the heat of reaction of the sample has been derived theoretically by several investigators, Speil (1944), Speil, *et al.* (1945), Kerr and Kulp (1948), and

---

[1] Contribution from the Soil Science Department and approved for publication by the Director as Journal Article No. 2839 of the Michigan Agricultural Experiment Station, E. Lansing, Michigan.

Eriksson (1952, 1953, 1954). This method has been applied by Barshad (1952) in measurement of heats of inversion and melting of several pure compounds and also to heats of dehydration of certain clay minerals. On the other hand, Stone (1954), utilizing a variable pressure apparatus, has applied the Clausius-Clapeyron equation for determination of heats of dehydration and decomposition of clay minerals and magnesite.

This study was conducted to compare the two methods of determining ΔH.

EXPERIMENTAL METHODS

All differential thermal measurements were made using a variable pressure apparatus similar to that described by Stone (1960). The sample holder was a nickel alloy and the differential thermocouple Pt--Pt (90%) Rd (10%). The heating rate was maintained at 13±0.5° C. per minute in all measurements.

Two minerals were selected for this study, magnesite and kaolinite. The magnesite was a hand specimen of unknown origin. The kaolinite was a reference clay mineral from Lamar Pit, Number 5, Bath, South Carolina. Because the primary objective of this experiment was to compare two methods of determining heats of reaction, the minerals were used in their natural state except for grinding in a mortar. The purity of both minerals is reflected by the differential thermal curves shown in Fig. 1.

Method of Direct Calibration. The simplest method of determining heats of reaction through use of differential thermal analysis is by direct calibration of the instrument against materials with known heats of inversion, fusion and/or reaction. It was pointed out by Eriksson (1952) that the relationship between the heat evolved or absorbed by the sample and the area under the differential thermal analysis curve would depend upon the particular instrument used because changing the type or geometry of the sample holder would affect the heat flow within the sample and reference material. He suggested that the solution of the three dimensional equation for heat flow within a homogenous media adapted to the boundary conditions of each instrument would yield the maximum useful information concerning the relationship between the heat of reaction and area under the differential thermal analysis curve. This approach was utilized to determine which factors should affect a direct calibration of the instrument used in this investigation. It was found that the area under the differential thermal analysis curve should be directly proportional to the heat evolved or absorbed by the sample if the following boundary conditions could be maintained.

1. The heat conductivity of the sample holder must be much greater than that of the sample.

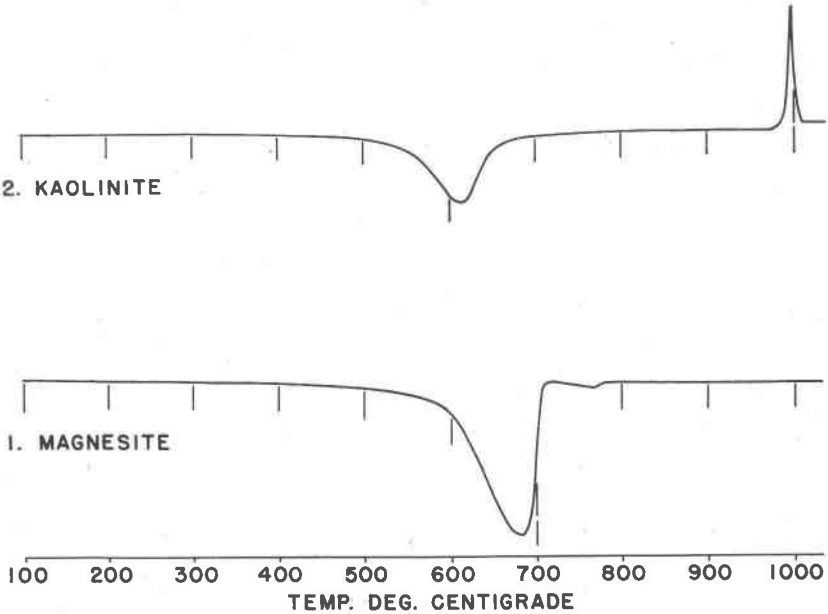

FIG. 1. Differential thermal analysis curves of magnesite and kaolinite.

2. The thermocouple must be centered in the sample.
3. The diffusivity of the sample must approach the diffusivity of the reference material.
4. Heat production within the sample must be uniform with respect to the vertical axis. The vertical heat flow must be negligible in comparison to the horizontal heat flow.

The first two boundary conditions are inherent with the instrument. The first is a good approximation for metal sample holders with a high thermal conductivity. It should be noted that this assumption would not be valid for ceramic sample holders. The second boundary condition is easily maintained for cylindrical holes in the sample holder. The third restriction presents rather large difficulties when working with materials which vary considerably in heat capacity and thermal conductivity. To reduce this difficulty the samples studied were diluted with Al_2O_3 and then compared against Al_2O_3 as the reference material. The Al_2O_3 used was anhydrous aluminum oxide, Fisher Catalog No. A591. To prepare a uniform dilution with Al_2O_3 a small quantity of the material to be used was placed into a plastic vial and accurately weighed. After addition of Al_2O_3 to give the proper ratio of sample to Al_2O_3, the mixture was ground

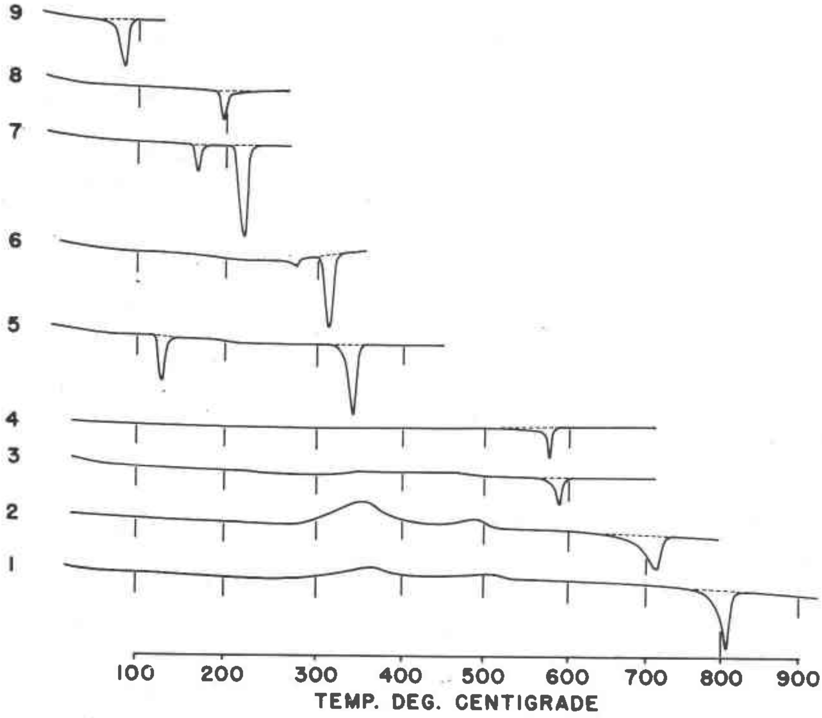

FIG. 2. Differential thermal analyses curves of materials used for heat of reaction calibration. 1) NaCl 8.93%, 0.226 g; 2) RbCl 22.7%, 0.232 g; 3) K_2SO_4 52.8%, 0.280 g; 4) quartz 100%, 0.283 g; 5) KNO_3 41.2% 0.215 g; 6) $NaNO_3$ 21.7%, 0.230 g; 7) $AgNO_3$ 53.0%, 0.273 g; 8) NH_4Cl 17.2%, 0.208 g; 9) m-dinitrobenzene 32.7%, 0.185 g.

with a Wig-L-Bug dental grinder for a period of five minutes. The assumption that the heat production is uniform with respect to the vertical axis should be valid if the sample is symmetrical with respect to the vertical axis and the diffusivity of the sample is uniform. It is then evident that the vertical heat flow gradient is small. Barshad (1952) found that a sample placed a short distance from the thermocouple produced a much smaller area than an equal quantity of material surrounding the thermocouple. This shows that the principal heat flow is along horizontal planes even when a vertical heat gradient exists. To further reduce the vertical heat flow the sample was insulated on both top and bottom by 1.5 mm of Al_2O_3 and capped on both top and bottom by porous disks.

Examples of differential thermal curves of the materials used for calibration are shown in Fig. 2. Several samples with different dilutions were used for each material except quartz. The range of per cent sample was from 4 to 55 per cent. The dotted extension of the base line is the line used to enclose the area of the particular peak. It was drawn to include all of the area from the point where the curve departed from the base line until it returned to the base line.

The calibration curve obtained is given in Fig. 3. The heat of reaction data except for KNO_3 were obtained from the National Bureau of Standards Circular 500. A discrepancy of the data for KNO_3 appeared between these tables and the Handbook of Chemistry and Physics. The value used for KNO_3 in this calibration was 2.28 kilocalories per mole as given in the Handbook of Chemistry and Physics. The area under the curve was determined by tracing the curve on drawing paper of uniform weight and cutting out the inscribed area. The weights of the cutouts were subsequently determined by use of an analytical balance. Each area was cut out three times and an average of the three used. Each point represents an average of two determinations with the differential thermal analysis apparatus. It is felt that the deviation from the reactions occurring be-

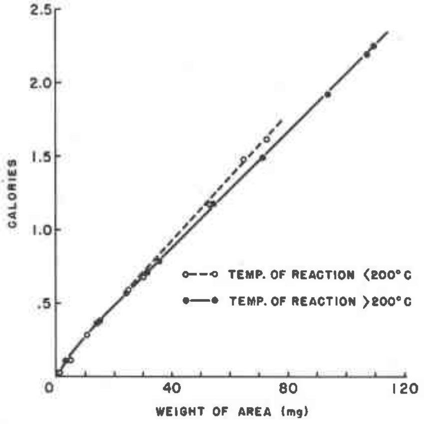

FIG. 3

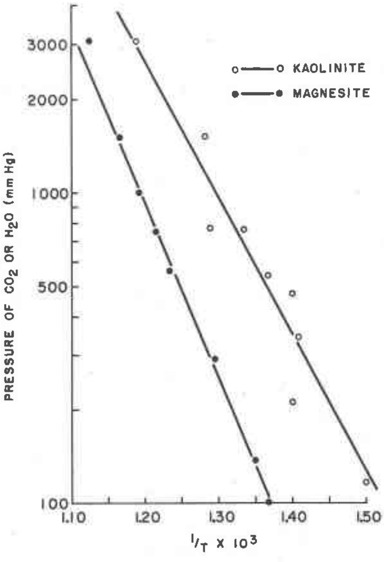

FIG. 4

FIG. 3. Calibration curve for heat of reaction versus area under the differential thermal analysis curve. One square cm weighs 16.7 mg.

FIG. 4. Relationship between decomposition pressure and temperature of magnesite and kaolinite.

low 200 degrees centigrade arises from a difference in the e.m.f. produced for a given temperature differential. This phenomenon has been discussed by Barshad (1952).

Clausius-Clapeyron Equation. It has been suggested by Stone (1954) that a differential thermal analysis instrument equipped to control the atmosphere and pressure surrounding the sample by use of a dynamic gas is very useful in determining heats of reaction by use of the Clausius-Clapeyron equation

$$\left(\ln P = \frac{-\Delta H}{R} \cdot \frac{1}{T} - C\right).$$

It should be noted that the following restrictions apply to the Clausius-Clapeyron equation:

1. Closed system.
2. Pressure-volume work only.
3. Reversible phase transition.
4. Ideal gas for the gas phase.
5. Volume of the gas phase much larger than the volume of the solid or liquid phase.

To apply this to differential thermal analysis the decomposition products must be accurately known, the pressure and composition of the gas surrounding the sample carefully controlled, and the temperature at the onset of the reaction determined precisely. In Fig. 4 the logarithm of pressure is plotted against the reciprocal of temperature (degrees Kelvin) at the onset of the decomposition for the two materials studied. The plot is linear as the Clausius-Clapeyron equation would predict. The scatter of points for the decomposition of kaolinite may be the result of difficulties in maintaining the gas surrounding the sample at 100 per cent saturation with respect to water vapor. The line for kaolinite was obtained by the method of least squares. The equation for this line is $\log (P_{H_2O}) = -10.2 \times 10^3 (1/T) + 20.13$.

Comparison of the Two Methods. The comparison of the heats of decomposition and dehydroxylation of magnesite and kaolinite respectively are given in Table 1.

The decomposition of magnesite under variable CO_2 pressures was studied by Stone (1954), after which he proposed that the reaction was a straightforward decomposition as given below:

$$MgCO_3 \rightleftarrows MgO + CO_2.$$

Using the Clausius-Clapeyron equation, he calculated a ΔH of decomposition of 10.1 kilocalories per mole of magnesite. This is considerably

Table 1. Heat of Decomposition of Magnesite and Dehydroxylation of Kaolinite

Method	Magnesite (ΔH K cal/mole)	Kaolinite (ΔH cal/g.)
Calculated from heat of formation data	28.1	—
Determined from calibration curve	28.3	154
Determined by Clausius-Clapeyron equation	27.0	157

lower than the 27.0 kilocalories per mole given in Table 1 and the theoretical 28.1 calculated using heat of formation data obtained from the National Bureau of Standards Circular 500. It may be seen in differential thermal curves shown by Stone that the magnesite he was working with contained an impurity which he attributed to calcium carbonate. This may have caused the low value he obtained for the heat of decomposition of magnesite. As can be seen in Table 1 the two methods agree very well for magnesite and both are in close agreement with the theoretical value.

Values for the decomposition of kaolinite vary considerably from sample to sample. Van der Marel (1956) has reported values from 100 to 176 calories per gram and Stone and Rowland (1955) found values from 140 to 170 calories per gram of kaolinite depending on the source of the clay mineral. Consequently, no theoretical value is given for the ΔH of dehydroxylation of kaolinite. However, the values of 154 and 157 calories per gram obtained by the two methods are in very close agreement and in the range expected for dehydroxylation of kaolinite. It is highly questionable if the dehydroxylation of kaolinite can be considered reversible. This would suggest that the Clausius-Clapeyron equation should not be applied. The restriction of reversible phase transition which applies to the Clausius-Clapeyron equation raises from the assumption that the free energy in the gas phase is the same as the free energy of the solid or liquid phase. This is always valid for a reversible phase transition. If, on the other hand, the phase transition is not reversible, the free energy in each phase may approach each other or may be appreciably different. If they are appreciably different, the Clausius-Clapeyron equation will not be valid. It should not be assumed from the data presented for the heat of dehydroxylation of kaolinite that the Clausius-Clapeyron equation could be applied with success to other irreversible reactions.

SUMMARY

From the two materials tested, it would appear that either method is satisfactory. However, each system must be examined carefully before selecting the method to be used. For example, to apply the Clausius-

Clapeyron equation, the reaction must be well defined, produce a gas phase of known composition which may be supplied from an external source, and yield a single, reversible reaction. On the other hand, the method of area determination may be applied to any system in which the heat capacities and thermal conductivities change little during a reaction. However, this measurement yields only the net heat evolved or absorbed and may be very difficult to interpret if two or more reactions occur simultaneously.

REFERENCES

BARSHAD, ISAAC (1952), Temperature and heat of reaction calibration of the differential thermal analysis apparatus. *Am. Mineral.*, **37**, 667–694.

ERIKSSON, ERIK. (1952), Problems of heat flow in differential thermal analysis. *Kungl. Lantbrukshögskolans Ann.*, **19**, 127–143.

——— (1953), Problems of heat flow in differential thermal analysis. Part II. *Kungl. Lantbrukshögskolans Ann.*, **20**, 117–123.

——— (1954), Problems of heat flow in differential thermal analysis. Part III. *Kungl. Lantbrukshögskolans Ann.*, **21**, 189–196.

GRIMSHAW, R. W. AND A. L. ROBERTS (1953), The quantitative determination of some minerals in ceramic materials by thermal means. *Trans. Brit. Ceram. Soc.*, **52**, 50–61.

KERR, P. F. AND J. L. KULP (1948), Multiple differential thermal analysis. *Am. Mineral.*, **33**, 387–419.

KIYOURA, R. AND T. SATA (1950), The quantitative analysis of the $CaCO_3$-$Ca(OH)_2$-$Mg(OH)_2$ system by differential thermal analysis. *Jour. Ceram. Assoc. Japan*, **58**, 3–6.

MURRAY, J. A., H. C. FISCHER AND R. W. SHADE (1951), Thermal analysis of limestone. *Proc. 49th Ann. Conv. Natl. Lime Assoc.*, Washington.

NORTON, F. H. (1940), Analysis of high alumina clays by the thermal method. *Jour. Am. Ceram. Soc.*, **23**, 281–282.

SPEIL, S. (1944), Application of thermal analysis to clays and aluminous materials. *U. S. Bur. Mines, R. I.* **3764.**

———, L. H. BERKHAMER, J. A. PASK AND B. DAVIES (1945), Differential thermal analysis. *U. S. Bur. Mines, Tech. Paper* **664.**

STONE, R. L. (1954), Thermal analysis of magnesite at CO_2 pressures up to six atmospheres. *Jour. Am. Ceram. Soc.*, **37**, 46–47.

——— (1954), Preliminary study of the effects of water vapor pressure on thermograms of kaolinite soils. *Proc. Second Natl. Conf. Clays and Clay Minerals.*

——— (1960), Differential thermal analysis by the dynamic gas technique. *Anal. Chem.*, **12**, 1582–1588.

——— AND R. A. ROWLAND (1955), DTA of kaolinite and montmorillonite under water vapor pressure up to six atmospheres. *Proc. Third Natl. Conf. Clays and Clay Minerals.*

VAN DER MAREL, H. H. (1956), Quantitative differential thermal analysis of clays and other minerals. *Am. Mineral.*, **41**, 222–244.

Manuscript received, August 10, 1961.