TEMPERATURE AND HEAT OF REACTION CALIBRATION OF THE DIFFERENTIAL THERMAL ANALYSIS APPARATUS

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ABSTRACT

Differential thermal curves representing one or several substances of known melting or inversion points, and of known heats of fusion or decomposition are proposed as a means for a direct temperature and heat of reaction calibration of the differential thermal analysis apparatus. Excellent agreement between determined and calculated heats of reaction of several substances attested to the validity of the derivation relating peak area of a thermal break to the heat of reaction causing the break. The proposed calibration imparts to *d.t.a.* curves constant parameters and consequently curves obtained with different instruments become comparable. The heat of reaction calibration enables a direct determination of the heat quantities involved in desorption or sorption of liquids on clay minerals—namely *the integral heat of desorption and the integral net heat of desorption.*

It is widely recognized that due to several factors inherent in the instrumentation of the *d.t.a.* apparatus (1, 5), the *d.t.a.* curves of minerals are not strictly constants. The deviation from constancy appears to be in all the parameters defining the thermal breaks in a *d.t.a.* curve—namely, initial temperature, peak temperature, peak height, peak range, and peak area. Of these parameters, the initial temperature—the lowest temperature at which the reaction could occur—and the peak area—which is proportional to the heat involved in the reaction causing the thermal break—(6, 10) are the most important. A simple calibration, therefore, of the *d.t.a.* apparatus which would yield constants for these two parameters would enhance greatly the usefulness of *d.t.a.*

The methods in use for recording the temperature scale on a *d.t.a.* curve involve generally a temperature thermocouple in circuit with a temperature recorder which are entirely separated from the differential thermal recording circuit.

Only a limited amount of work has appeared suggesting methods for calibrating the *d.t.a.* apparatus for evaluating heats of reaction. Wittels' method (11, 12) of using the decomposition of $CaCO_3$ as a means for calibration is so far the most useful, but it is limited to a narrow range of temperature and small amounts of material.

The purpose of the present paper is to suggest methods whereby the differential thermal circuit itself may be utilized to obtain calibrated temperature and heat of reaction scales. The methods consist in obtaining *d.t.a.* curves of organic and inorganic substances of known melting and/or inversion points and of known heats of fusion and heats of decomposition. The usefulness of such *d.t.a.* curves lies in that at the instant of melting, inversion, or decomposition, an endothermic break appears the initial point of which marks the temperature of fusion, inversion, or decomposition and the area of which is proportional to the heat of fusion, inversion or decomposition. In the present paper substances used for the heat of reaction calibration are termed temperature indicators.

EXPERIMENTAL

Temperature Calibration

The equipment used was as follows: the sample holder consisted of a rectangular nickel block with dimensions 23×23×15 mm. and with two holes—7 mm. in diameter and 13 mm. in depth—capable of holding 0.55 gm. of tightly packed Al_2O_3. A cover for the block was not used. Platinum—platinum (90%) rhodium (10%) thermocouples were employed and the recorder consisted of a reflecting galvanometer on photographic paper. All of the experiments were conducted with the galvanometer adjusted to a sensitivity so that at 100° C. a temperature difference of 10° C. produced a deflection of 10 cm.

The base line on which to record the temperature scale is obtained while the galvanometer is resting at the null position and the furnace turned off. The spot of light marking the photographic paper, through its reflection in the galvanometer mirror, is turned on while the drum holding the photographic paper is rotated. A short pause at two or three positions leaves points through which the base line may be drawn.

For a given thermal reaction the galvanometer may be made to deflect the spot of light either upward or downward from the base line depending on the position of the reacting sample with respect to the two thermocouples. In general practice in *d.t.a.*, the deflection due to an endothermic reaction is directed downward and that due to an exothermic reaction upward from the base line. However, in the experiments reported herein, the deflection for a given thermal reaction was made in either direction of the base line depending solely on the position of the sample with respect to the two thermocouples.

For a thermal reaction to be of value as a fixed temperature reference point, it should impress on a *d.t.a.* curve an abrupt break.

To find a method whereby the whole temperature scale could be established with one *d.t.a.* curve having several temperature reference points, several of the factors which may affect the position of a fixed temperature-reference-point on a *d.t.a.* curve were investigated. These were: (1) The rate of heating, (2) The initial temperature, and (3) The existence of temperature differences within the sample holes due to position with respect to the thermocouples.

(1) In most *d.t.a.* apparatus the rate of heating determines directly

the linear dimensions of the temperature scale. A change, therefore, in the rate of heating would alter the temperature scale. Maintenance of a characteristic rate of heating will insure usually a constant temperature scale. Occasionally, however, due to variation in line voltage, the rate of heating alters somewhat, and consequently the scale also alters. If such a situation persists a method will be suggested whereby the temperature scale may be recorded directly on the *d.t.a.* curve of a test sample.

(2) Variations in the initial temperature of the furnace would affect the time of occurrence of a reaction which marks a temperature reference point. Consequently, the position of the point on a scale would vary with the initial temperature. This difficulty may be eliminated by starting the temperature scale from a fixed temperature reference point. Such a reference point is found in the first inversion reaction of NH_4NO_3 occurring at 32° C. Where summer temperatures exceed 32° C. the second inversion point of NH_4NO_3 occurring at 85° C. may be chosen as the initial reference point of the scale. By this method any desired portion of the temperature scale may be delineated by a judicious choice of reference points.

(3) To ascertain the existence of temperature differences in the sample holes due to position with reference to the thermocouple a *d.t.a.* was made of small amounts of an indicator placed at two positions in the sample hole. The appearance of only one reference point in the *d.t.a.* curve as in the curve of $AgNO_3$ (Curve *A*, Fig. 1) indicates that at any given moment the temperature is uniform throughout the sample hole. The same method was utilized to ascertain whether the two differential thermocouples are being heated at the same rate. In this case, however, the same indicator was placed in both sample holes but with one of the holes containing a slightly larger amount of the indicator than the other. The appearance of only one reference point for each reaction as in the curve for NH_4NO_3 (Curve *B*, Fig. 1) indicates that the rise in temperature is identical for the two holes.

The uniform rise in temperature within the sample holes during *d.t.a.* enabled the development of a method for ascertaining the whole of the temperature scale with a single *d.t.a.* curve. The method consists in making a *d.t.a.* simultaneously of several indicators which are placed either around one or both of the differential thermocouples in narrow layers separated by Al_2O_3 as shown in Figs. 3 and 4. The resulting *d.t.a.* curve possesses several thermal breaks which mark the fixed temperature reference points characteristic of each indicator.

The amount of each indicator to be used for such an analysis was found to depend upon the sensitivity of the *d.t.a.* apparatus, the magnitude of

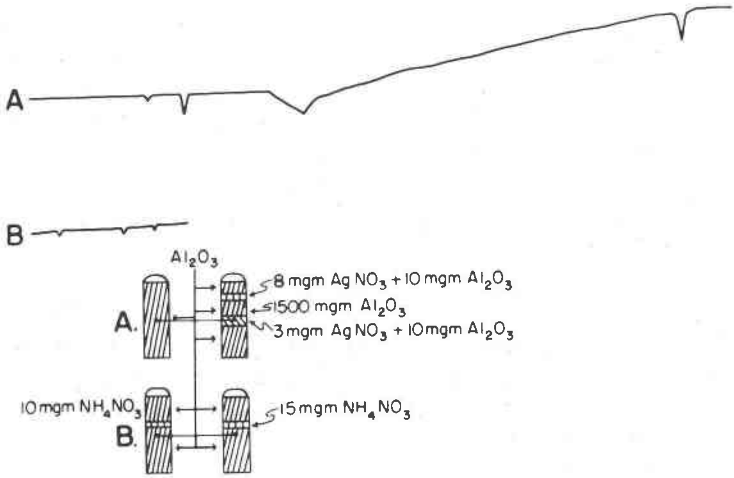

FIG. 1. *D.t.a.* curves of $AgNO_3$ placed at two positions in the same sample hole and of NH_4NO_3 placed at the two thermocouples.

the heat of fusion or inversion of the indicator, and upon the position of the indicator in the sample hole with respect to the thermocouple junction. For example, it was found that an instrument having a sensitivity of a 10 cm. deflection for a 10° C. difference in temperature will register a large enough thermal break to mark a temperature reference point with an amount of 2 mgm. of an indicator having a heat of fusion or inversion of 20 to 30 calories per gram when placed right around the thermocouple junction. However, placing the indicator at a distance of about 4 to 5 mm. from the junction increased the required amount of indicator from 2 to 10 mgm. The indicators should be powdered before use and when placed in direct contact with the thermocouples they should be mixed with about 10 mgm. of Al_2O_3 to prevent them from sticking to the junction and wires upon fusion.

TABLE 1. PEAK AREA OF THE ENDOTHERMIC BREAK IN *d.t.a.* CURVES OF 50 MGM. OF KAOLINITE PLACED AT DIFFERENT POSITIONS* WITH RESPECT TO THE THERMOCOUPLE

Position of sample	Peak area
	cm.^{2}
5.5 mm. above thermocouple	0.68
3.0 mm. above thermocouple	1.80
0.0 mm. from thermocouple	3.24
3.5 mm. below thermocouple	1.21
6.0 mm. below thermocouple	0.40

* To place sample in desired position proper amounts of Al_2O_3 were used as the "filler" for the bottom and top portions of the sample hole.

The dependence of the magnitude of the thermal break of a given amount of indicator upon its distance from the thermocouple junction is shown in Fig. 5 and Table 1. It is seen that the magnitude of the deflection or the peak area are smaller the greater the distance of the reacting substance from the thermocouple junction. With the size holes used in the present experiments, the endothermic reaction occurring in the indicators placed in the bottom of the hole or near its top hardly induced a thermographic response. An exception, however, to this observation are the large exothermic breaks in the *d.t.a.* curves of all of the NH_4NO_3 samples placed below the thermocouple junction. The cause for this exception appears to be in the nature of the exothermic reaction responsible for this exothermic break. The reaction involves a platinum catalyzed oxidation of NH_3 liberated during the decomposition of NH_4NO_3. The presence of larger exothermic breaks in the curves of the samples placed below the thermocouple than in those placed above the thermocouple, results from the larger amounts of NH_3 which must diffuse upwards past the thermocouple from the former than from the latter samples.

It would appear, therefore, that in using NH_4NO_3 as an indicator, either with other indicators or with unknown subtances, to mark the beginning of the temperature scale it would be advisable to limit the exothermic reaction to a minimum so as not to mask any other reaction which might occur in that temperature range. This can be accomplished by placing the NH_4NO_3 about 2 to 3 mm. above the thermocouple junction and limit its amount to about 2 or 3 mgm. For marking the temperature scale in the *d.t.a.* curves of test samples it was found more desirable to place the NH_4NO_3 with the reference sample rather than with the test sample.

The substances found useful for the temperature and the heat of reaction calibration are listed in Table 2, together with their melting and/or inversion temperature points, their heats of fusion or inversion, and the amounts needed in calibration. The individual *d.t.a.* curves of some of these substances are shown in Fig. 2. Among the substances tested, NH_4NO_3 and $AgNO_3$ are among the most useful. The usefulness of NH_4NO_3 lies in the temperature range below 170° C.; it is particularly valuable as an indicator for marking the beginning of the temperature scale. The usefulness of $AgNO_3$ lies in its ability to mark three temperature points, namely 160° C., 212° C., and 960.5° C., from which the whole temperature scale above 160° C. may be constructed if the rate of heating is constant throughout this temperature range. AgI and Ag_2SO_4 are also among the more useful indicators, for they too mark more than one temperature point. AgI marks points at 147° C. and 554° C., and Ag_2SO_4 marks points at 432° C., 652° C., and 960.5° C.

TABLE 2. MELTING AND INVEFSION TEMPERATURES AND HEATS OF FUSION OF SUBSTANCES USEFUL FOR TEMPERATURE AND HEAT OF REACTION CALIBRATION OF THE *d.t.a.* APPARATUS (3, 7)

Substance	Point*	Temperature	Heat of fusion	Amount for temperature calibration	Amount for heat reaction calibration
		°C.	cal./gm.	mgm.	mgm.
NH_4NO_3	I	32		2–10	
NH_4NO_3	I	85			
NH_4NO_3	I	125			
NH_4NO_3	M	170			
KNO_3	I	128		2–10	
m-Dinitrobenzene	M	90	24.7	2–10	50–100
o-Dinitrobenzene	M	117	32.3	2–10	50–100
Benzoic Acid	M	122	33.9	2–10	50–100
$AgNO_3$	I	160		2–10	
$AgNO_3$	M	212	16.7	2–10	50–100
Ag (from $AgNO_3$)	M	961	25.0	2–10	50–100
AgI	I	147		20–40	
AgI	M	552		20–40	
Ag_2SO_4	I	432		20–40	
Ag_2SO_4	M	652		20–40	
Ag (from Ag_2SO_4)	M	961		20–40	
AgCl	M	307		1–10	50–100
$NaNO_3$	M	314	45.3	1– 5	50–100
$NaMo_2O_4$	I	642		5–10	
	M	687		5–10	
NaCl	M	804		2– 5	20– 50
K_2SO_4	I	583		5–10	
Quartz	I	573		10–50	

* Inversion = I, Melting = M.

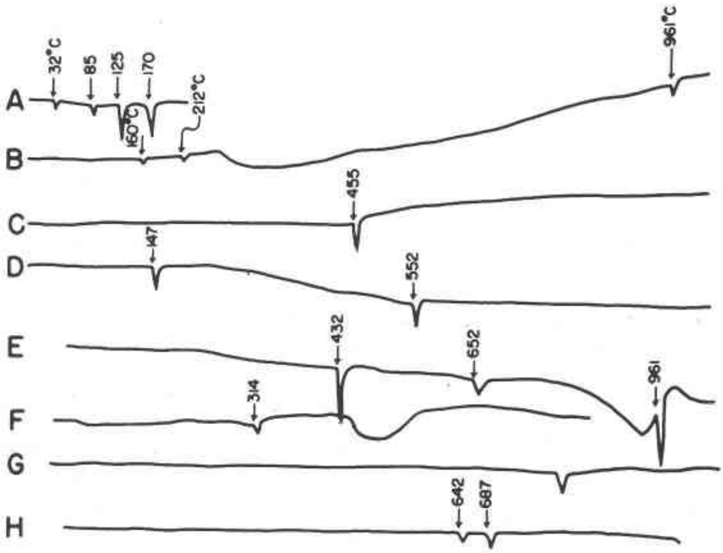

FIG. 2. *D.t.a.* curves of salts useful for temperature calibration. The salts were dispersed in 10 mgm. of Al_2O_3 and centered around the thermocouple.

A. 10 mg. NH_4NO_3
B. 3 mg. $AgNO_3$
C. 2 mg. AgCl
D. 15 mg. AgI
E. 20 mg. Ag_2SO_4
F. 2 mg. $NaNO_3$
G. 2 mg. NaCl
H. 3 mg. $Na_2Mo_2O_4$

When the indicators are mixed prior to *d.t.a.* some retain their identity whereas others do not—the latter assume forms which are the result of interaction of the indicators or their reference points may disappear completely. Thus, when $AgNO_3$, AgCl, AgI, Ag, and quartz are mixed, the identity of each is retained but when NH_4NO_3, AgCl, $AgNO_3$, and $Na_2Mo_2O_4$ are mixed, the former two retain their identity, whereas the latter two do not. It would appear, therefore, that those indicators which do not interact may be mixed prior to anlaysis but those which do should be placed in the sample holes as single layers separated by Al_2O_3. Some of the mixed indicators tested are shown in Figs. 3 and 4.

The method of placing the temperature indicators in narrow layers has its greatest utility in making it possible to register on a *d.t.a.* curve of a test sample the whole or any desired part of the temperature scale. By this means it becomes possible to define a thermal break of a test sample very accurately regardless of inconsistencies which may occur in the *d.t.a.* apparatus. Several such marked curves were obtained of various minerals and with various rates of heating (Figs. 6*a*, 6*b*, 6*c*, and 6*d*). These curves show that the rate of heating had no effect on the temperature defining the initial thermal breaks.

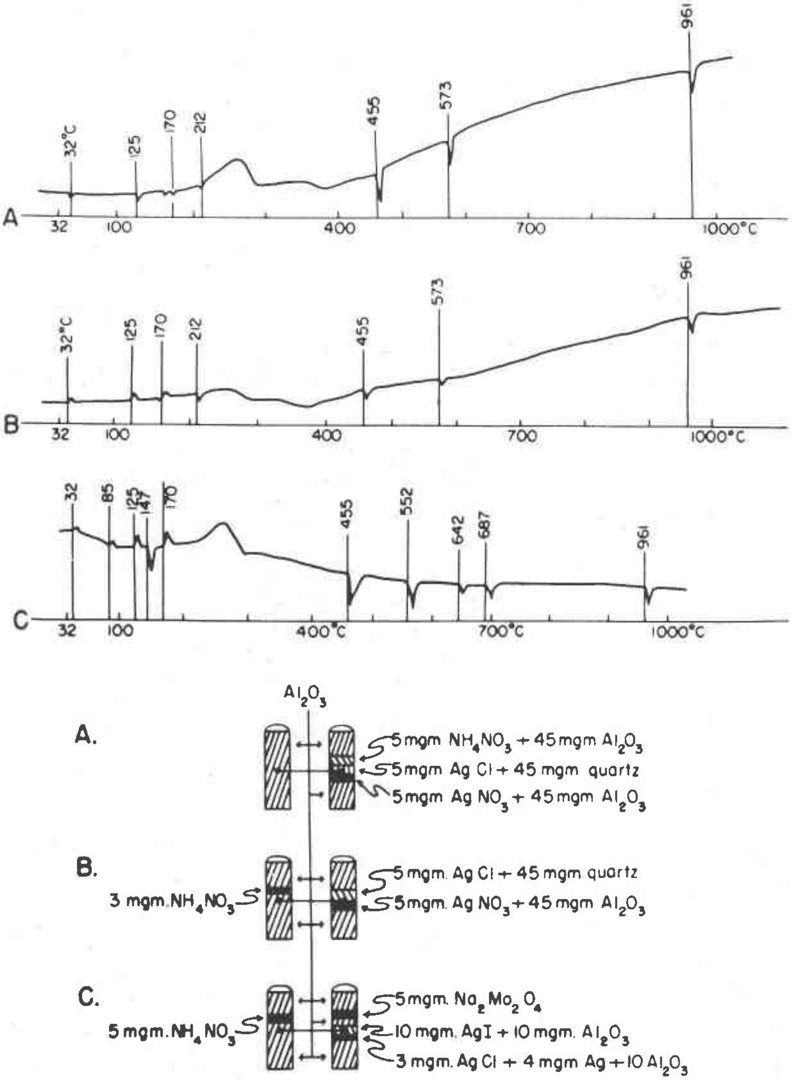

FIG. 3. Curves resulting from simultaneous *d.t.a.* of several substances placed in layers in the sample holes.

The temperature indicators were also found useful in evaluating the sensitivity of the *d.t.a.* apparatus. The method consists in placing in one of the sample holes a material which produces a large endothermic break, in the center of which, right around the thermocouple, is embedded an indicator which registers a temperature reference point near the peak of the endothermic break of the surrounding sample. At the same time one or two indicators are embedded in the reference material which

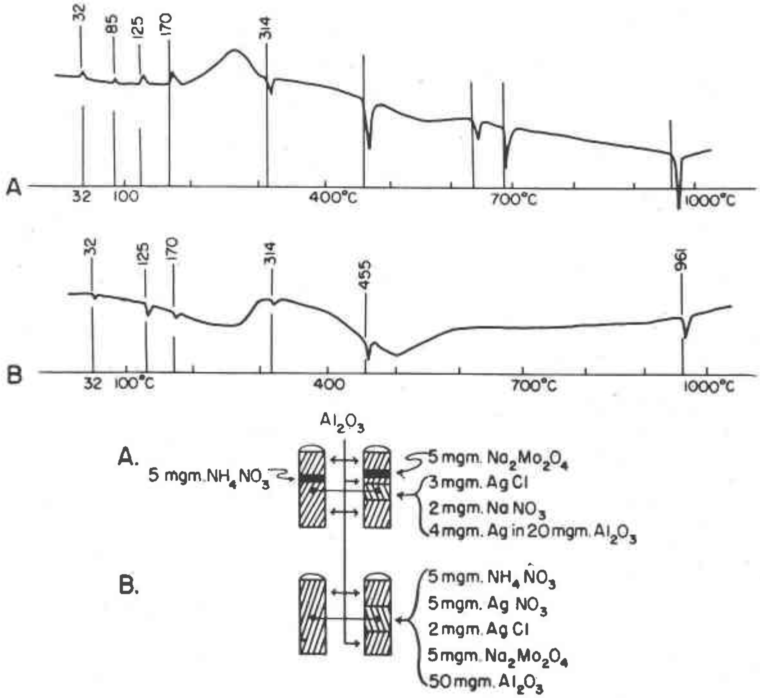

FIG. 4. Curves resulting from simultaneous *d.t.a.* of several substances mixed prior to analysis.

register one reference point preceding and one following the reference point registered by the indicator embedded in the test sample. From the former two points, the temperature in the inert sample at the time the latter point is registered may be ascertained. This determination yields the temperature difference between the thermocouples caused by the endothermic reaction in the test sample. The sensitivity is then obtained by dividing this temperature difference to the peak height at that point in the curve. Ca-montmorillonite was found useful as the test sample at the low temperatures and kaolinite at the higher temperatures. The two temperature points which AgI registers in the *d.t.a.* curve enables it to act as the indicator to be embedded in both of these test samples. The three temperatures which NH_4NO_3 registers make it the suitable indicator to be embedded in the inert sample that is coupled with the Ca-montmorillonite. AgCl and $Na_2Mo_2O_4$ placed in two layers around the junction in the inert material are the suitable indicators to be coupled with the kaolinite. Figure 7 illustrates the curves obtained with these materials and the calculations involved in the determination of the sensitivity.

The sensitivity at 100° C. may be determined without indicators by

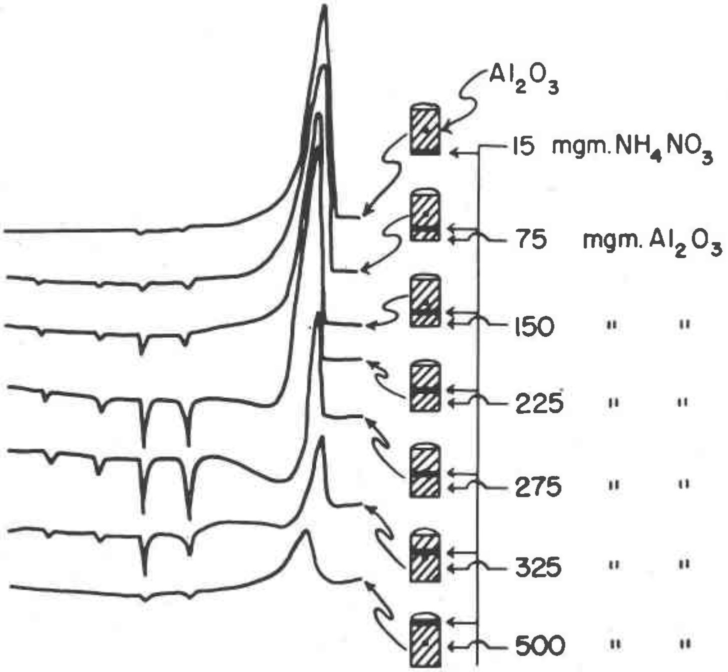

FIG. 5. *D.t.a.* curves of 15 mgm. of NH_4NO_3 placed at different positions with respect to the thermocouples.

the following method which requires two operators. Each of the thermocouples, while in the *d.t.a.* circuit, is placed in a separate beaker of boiling water standing on a small electric hot plate by the *d.t.a.* apparatus. While one operator places a precision mercury thermometer in one of the beakers of boiling water, the other operator observes the galvanometer until it attains a steady state at the null position. A thin sheet of asbestos is then placed under the beaker holding the thermometer. The drop in temperature in the beaker is read off and the change in the position of the light beam is marked on a sheet of paper placed in the position normally occupied by the photographic paper. To measure the sensitivity in the opposite direction of the null point, the foregoing procedure is repeated but with the second beaker being cooled while the first one is kept boiling.

These results are plotted as temperature differences vs. centimeters-deflection curves and converted into e.m.f. vs. centimeters-deflection curves with the aid of the standard calibration tables (4) for the thermocouples in use. These curves together with e.m.f. vs. hot-junction-temperature curves for various temperature differences between the thermo-

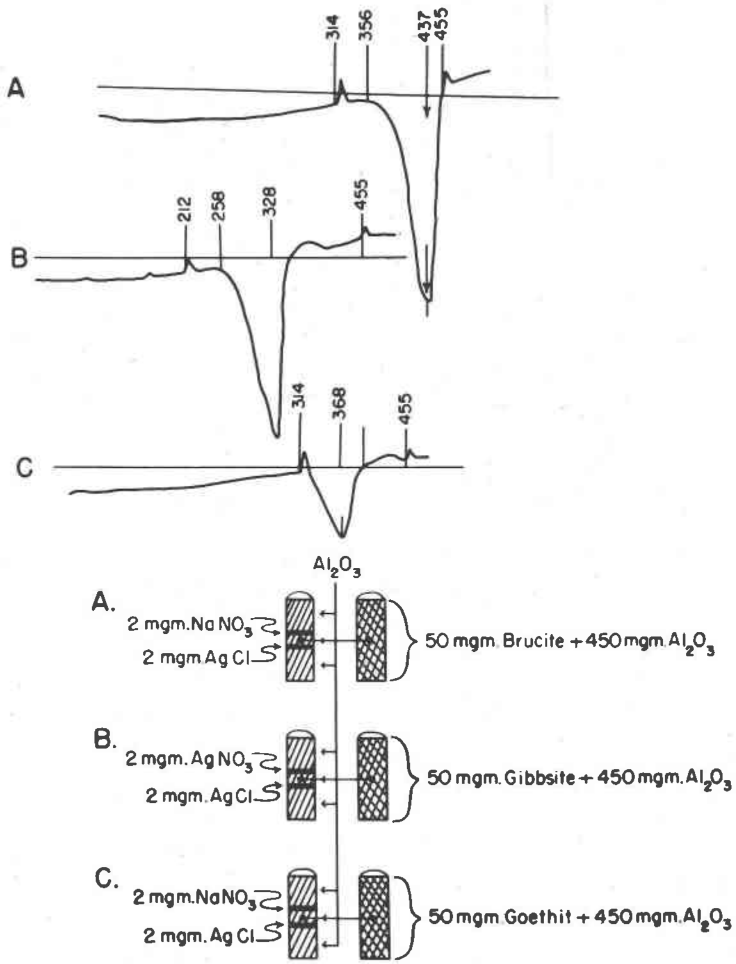

FIG. 6*a*. *D.t.a.* curves of brucite, gibbsite, and goethite with impressed temperature-reference points.

couples (Fig. 8) can be used to determine the sensitivity of the *d.t.a.* instrument at any hot-junction temperature other than 100°C. The determination consists in converting the extent of deflection at a given temperature into e.m.f. values by using the e.m.f. vs. centimeter-deflection curves; the e.m.f. values can then be converted into a temperature difference with the aid of the e.m.f. vs. hot-junction-temperature curves for various temperature differences. The following example illustrates such a determination of the sensititivity at 550° C. from the known sensitivity at 100° C. for a 10 cm. deflection taking place at 550° C. Since a

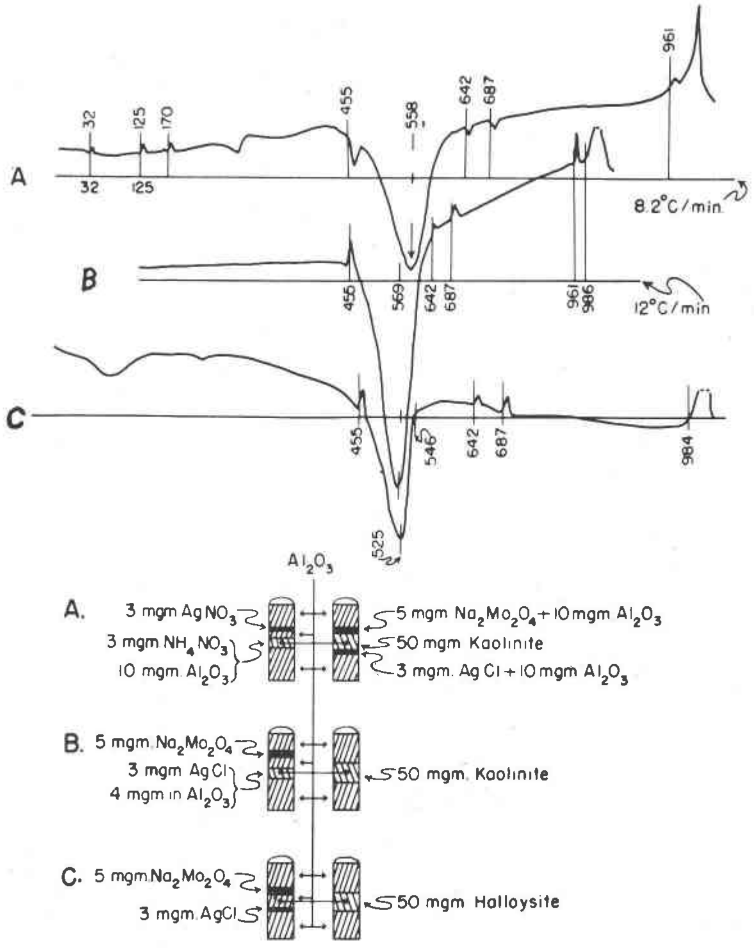

FIG. 6*b*. *D.t.a.* curves of kaolinite and halloysite with impressed temperature-reference points.

given deflection is produced by a given e.m.f. regardless of the temperature at which it takes place, it is found from the calibration curves obtained at 100° C. that the 10 cm. deflection is produced by a e.m.f. of 0.143 millivolt. At a hot-junction temperature of 100° C. such a e.m.f. represents a 10° C. difference in temperature. But at a hot-junction of 550° C., a 10° C. difference in temperature produces an e.m.f. of 0.200 millivolt. Therefore an e.m.f. of 0.143 millivolt at 550° C. is produced by a temperature difference of $10 \times 0.143/0.200$ or 7.2° C. The sensitivity, therefore, at 550° C. is equal to 7.2° C. per 10 cm. deflection.

Two temperatures are associated with the peak of a thermal break in

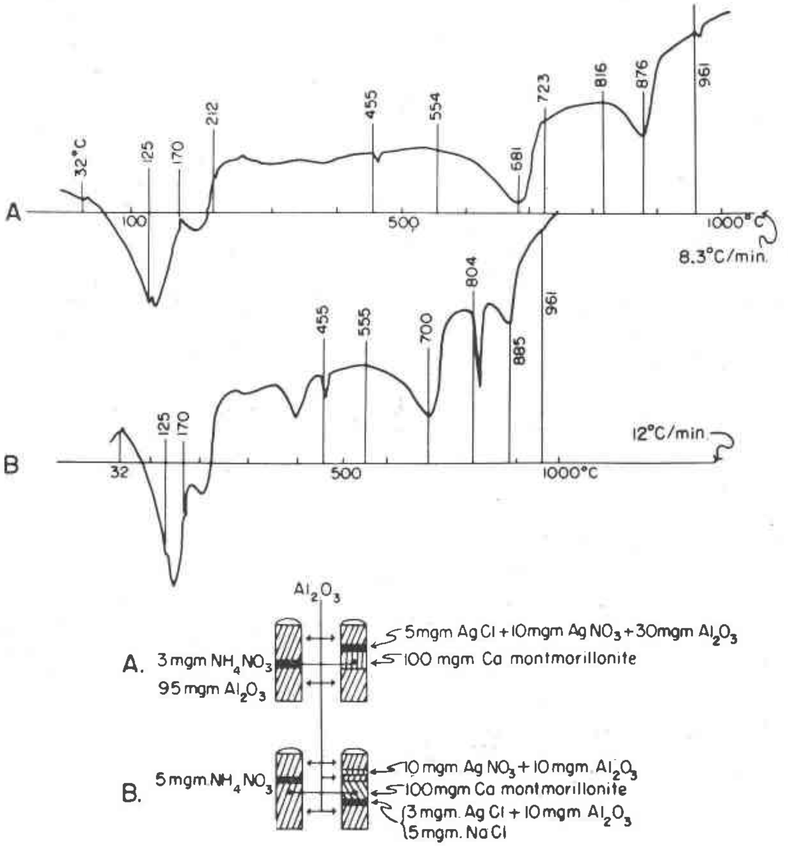

FIG. 6*c*. *D.t.a.* curves of a Ca-montmorillonite with impressed temperature-reference points.

a *d.t.a.* curve of a test sample—the temperature in the reference sample and the temperature in the test sample. Knowing the sensitivity of the instrument and the temperature scale for the reference material, both of these temperatures may then be determined.

Heat of Reaction Calibration

The dependence of the peak area on the heat of reaction in *d.t.a.* curves was derived theoretically by several investigators (1, 6, 10), therefore, the derivation need not be repeated here. Although the peak area representing a reaction in a definite amount of material is affected by various factors inherent in the *d.t.a.* apparatus (1, 5)—such as rate of heating, nature of sample holder, size of holes in sample holder, nature of thermocouples, and sensitivity of galvanometer—nevertheless a heat of reac-

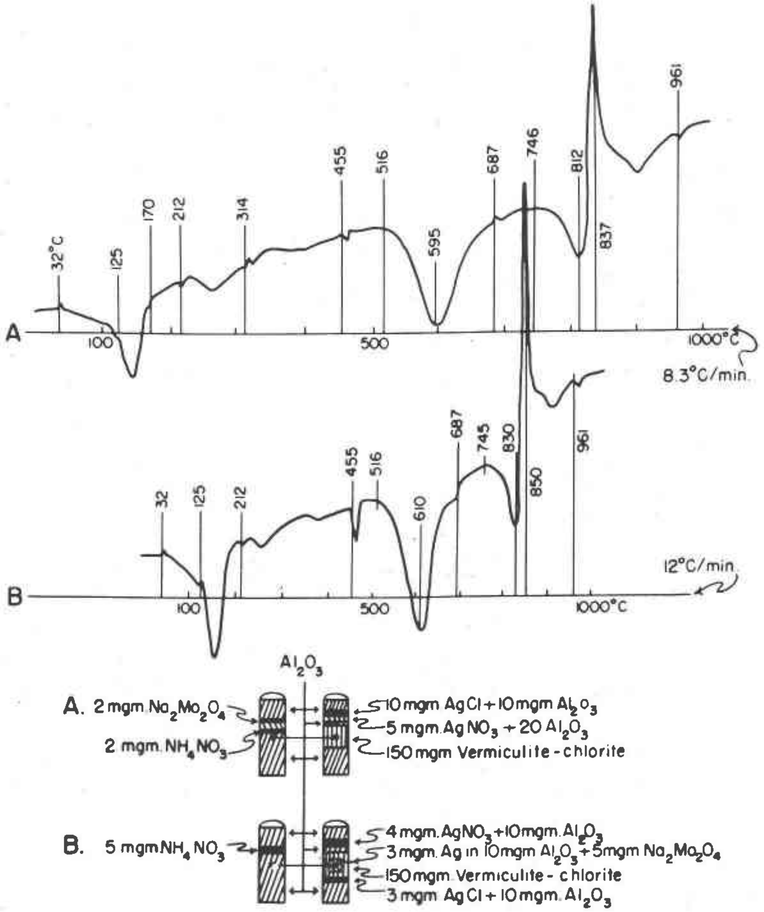

FIG. 6*d*. *D.t.a.* curves of a vermiculite-chlorite with impressed temperature-reference points.

tion determination, may be made possible provided the conditions existing in the *d.t.a.* apparatus at the time of calibration are maintained during analysis of unknown samples.

Some of the indicators found suitable for temperature calibration were found also suitable for the heat of reaction calibration, but to obtain accurately measurable peak areas much larger amounts of the indicators wree needed.

Since the indicators are mixed with an inert material, like Al_2O_3, to prevent them from sticking to the thermocouple junction at time of fusion, an investigation was made of the effect of the proportionality between the indicator and the inert substance on the peak area.

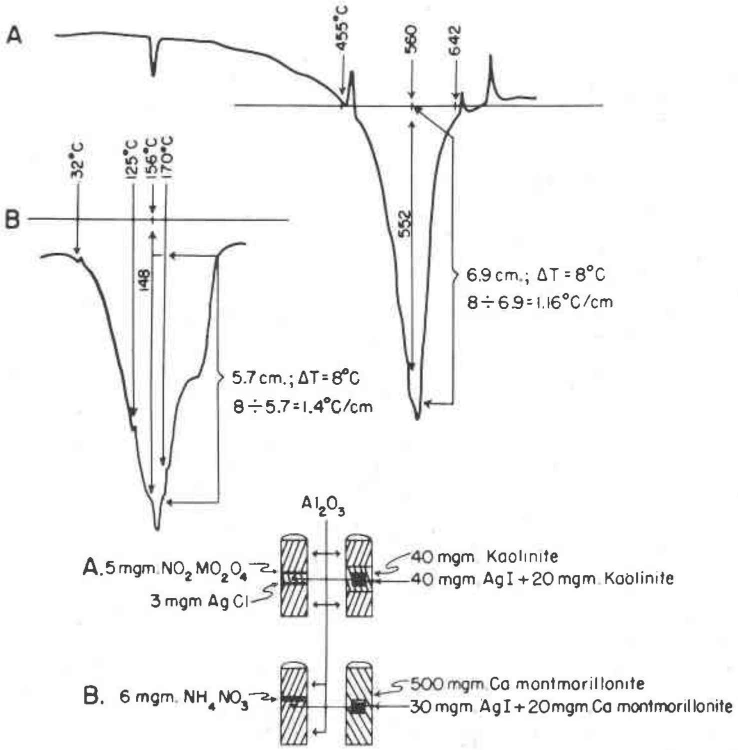

FIG. 7. *D.t.a.* curves of a Ca-montmorillonite and a kaolinite with impressed temperature-reference points suitable for measuring the sensitivity of the *d.t.a.* apparatus.

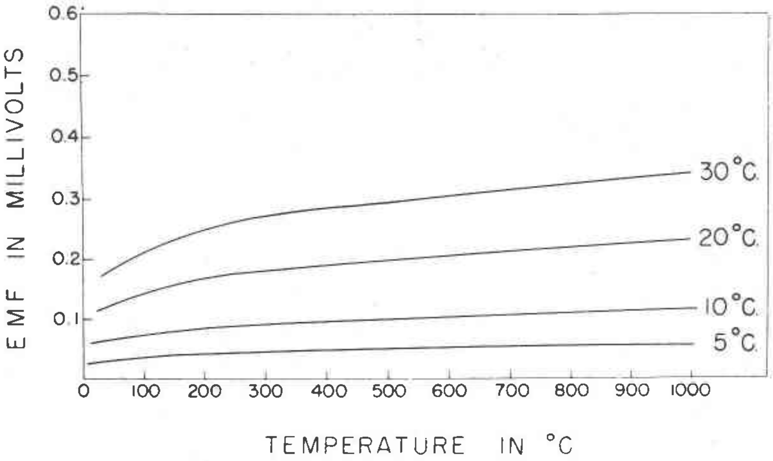

FIG. 8. E.M.F. vs. hot-junction-temperature curves for temperature differences of 5°, 10°, 20°, and 30° C. between the hot and cold thermocouples consisting of Pt-Pt (90%) Rh (10%).

Two methods were employed to obtain various proportions between the indicator and the inert substance. On the one hand a given amount of indicator was dispersed in increasing amounts of Al_2O_3 and consequently the mixture occupied an increasing volume. On the other hand increasing amounts of indicator were dispersed in decreasing amounts of Al_2O_3 in such manner that the mixture retained a constant volume. The results of the first method are shown in Table 3 and those of the second

TABLE 3. PEAK AREA OF THE ENDOTHERMIC BREAK IN THE *d.t.a.* CURVES OF 50 MGM. OF KAOLINITE DISPERSED IN AN INCREASING VOLUME AND CENTERED* AROUND THE THERMOCOUPLE

Volume of sample	Peak area
$cm.^3$	$cm.^2$
.040	4.06
.130	3.02
.220	2.55
.310	2.23
.400	1.94
.490	1.62

* To center the sample around the thermocouple proper amounts of Al_2O_3 were used as the "filler" for the bottom and the top portions of the sample hole.

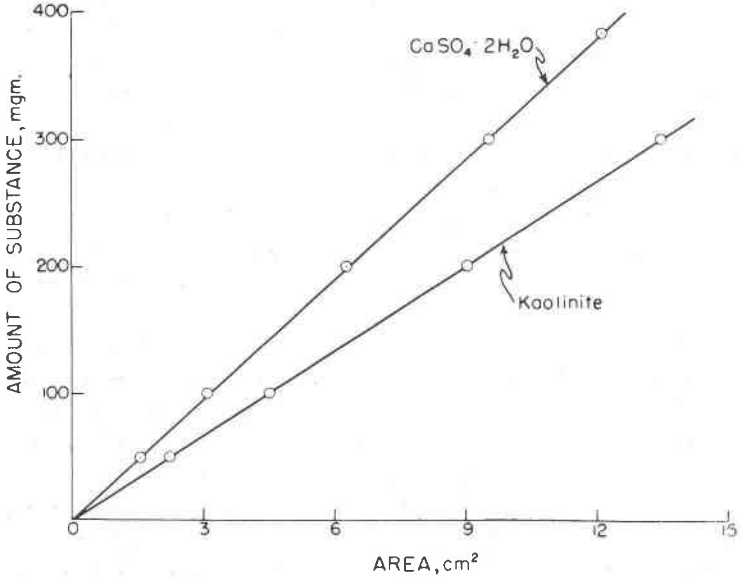

FIG. 9. Peak areas of the endothermic breaks in *d.t.a.* curves of various amounts of kaolinite and $CaSO_4 \cdot 2H_2O$.

method are shown in Figure 9. It is seen that the peak area for a given amount of indicator decreased as the volume which it occupied increased (Table 3), but the peak area for a given amount of indicator remained constant when dispersed in a constant volume. The decrease in the first instance is probably brought about by the increase in distance from the thermocouple of a portion of the indicator as it occupied a larger volume. For, as was shown previously, the peak area and amplitude for a reaction in a given amount of substance is inversely proportional to the distance of the indicator from the thermocouple. Consequently it would appear that the proportionality between the indicator and the inert substance is of little significance as long as the indicator is dispersed in a constant volume; and that in determining a heat of reaction in an unknown sample it should be confined to the same volume and placed in the same position with respect to the thermocouples as the indicator during calibration.

Since the indicators and test samples may vary considerably in their real and apparent densities, the dispersion in a constant volume may be achieved by first placing the desired amount of a substance in a hole of desired volume (made in piece of metal) and filling the remainder of the hole with Al_2O_3 which is packed to the same tightness as for *d.t.a.* The contents are then removed from the hole, mixed thoroughly and placed in the hole of the sample holder of the *d.t.a.* apparatus for analysis.

In using *d.t.a.* to estimate minerals like kaolinite, calcite, or others in unknown samples, the calibration curves of the standard minerals should appear as a plot of the actual quantity of the mineral used vs. the peak area obtained. The peak area in a *d.t.a.* curve of an unknown sample determined from such a calibration curve would correspond, therefore, to a definite quantity of the known mineral. To express this quantity on a percentage weight bases, the amount of the unknown sample used in *d.t.a.* must be known.

The absence of a thermographic response to a thermal reaction in the portion of the sample placed at a large distance from the thermocouple junction, as was shown previously, would suggest that this portion of the hole may be eliminated without affecting the intensity of the thermographic response. Seemingly the hole in the sample holder may be limited to such a size that a reaction in the remotest portion of the sample from the thermocouple would register a fairly strong thermographic response. In other words a small hole would be preferable to a larger one particularly when the recording instrument is of high sensitivity.

Since the sensitivity of thermocouples varies with the temperature, the heat involved in a reaction occurring in a test sample at a specific temperature range, may best be evaluated by using in calibration an indicator registering a thermal reaction at about the same temperature as that of the test sample. Moreover, in order that the calibration with a given indicator should apply to a fairly wide range of temperature. small amounts of the indicator rather than large ones should be used so that only small differences in temperature between the thermocouples would develop. For, as seen in Fig. 8, the smaller the difference in temperature between the thermocouples the smaller the variation in sensitivity of the thermocouples with temperature.

The following substances with known heats of fusion were found useful for the heat of reaction calibration: *m*-, *o*-dinitrobenzene, or benzoic acid in the temperature range between 25° C. and 150° C.; $AgNO_3$, $NaNO_3$, and AgCl in the temperature range between 150° C. to 500° C., and NaCl and Ag (derived from the decomposition of $AgNO_3$) in the temperature range between 500° C. and 1000° C. Other substances with known heats of fusion which have melting points at desired temperatures may be found just as satisfactory as those listed above.

In practice it is simpler to establish the heat of reaction scale in terms of calories per given weight of paper proportional to the peak area of a thermal reaction than in calories per given area. For it is considerably easier to cut out an area and weigh the paper than measure the area directly. However, the constancy in weight of a given area on a sheet of paper must be ascertained. Transparent millimeter paper of good quality was found satisfactory for this purpose.

The validity of the proposed calibration was tested by evaluating the heats involved in reactions, such as desorption of water from hydrated salts and decomposition of nitrates and carbonates, the values for which

TABLE 4. HEATS OF DECOMPOSITION OF $CaCO_3$, $AgNO_3$, AND $NaNO_3$ AS DETERMINED BY *d.t.a.* AND BY CALCULATIONS* FROM HEATS OF FORMATION (7)

Substance	Decomposition temperature in *d.t.a.*	Determined values	Calculated values	Decomposition temperature (t_2)
	°C.	Cal./gm.	Cal./gm.	°C.
$CaCO_3$	700–830	465	468	787
$AgNO_3$	370–470	212	210	400
$NaNO_3$	600–720	770	776	667

* The calculations were carried out for the following reactions (8)

$$CaCO_3 \rightarrow CaO + CO_2$$
$$AgNO_3 \rightarrow Ag + \tfrac{1}{2}N_2 + 1\tfrac{1}{2}O_2$$
$$NaNO_3 \rightarrow \tfrac{1}{4}Na_2O + \tfrac{1}{4}Na_2O_2 + \tfrac{1}{2}N_2 + 1\tfrac{1}{8}O_2$$

Lewis and Randall's (9) procedure was followed in calculating the temperature effect on these reactions but with the exception that ΔCp—the difference in heat capacities between reactants and products—was equated to the heat capacities of the liberated gases; since by the nature of *d.t.a.* the difference in the heat capacities of the solids is not measurable.

TABLE 5. INTEGRAL HEATS OF DESORPTION OF VARIOUS HYDRATED SALTS AS DETERMINED BY *d.t.a.* AND BY CALCULATION* FROM HEATS OF FORMATION

Salt	Determined values	Calculated values	Desorption temperature (t_2)
	Cal./gm.	Cal./gm.	°C.
$CaSO_4 \cdot 2H_2O$	164	160	140
$Ca(NO_3)_2 \cdot 4H_2O$	234	230	130
$BaCl_2 \cdot 2H_2O$	120	119	120
$MgSO_4 \cdot 7H_2O$	395	402	130
$SrCl_2 \cdot 6H_2O$	300	311	120
$Na_2S_2O_3 \cdot 5H_2O$	260	269	120

* The calculations were carried out for the following type reaction

$$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 + 2H_2O \text{ (gas)}.$$

The temperature effect on the reaction was calculated in the same manner as indicated in footnote to Table 4.

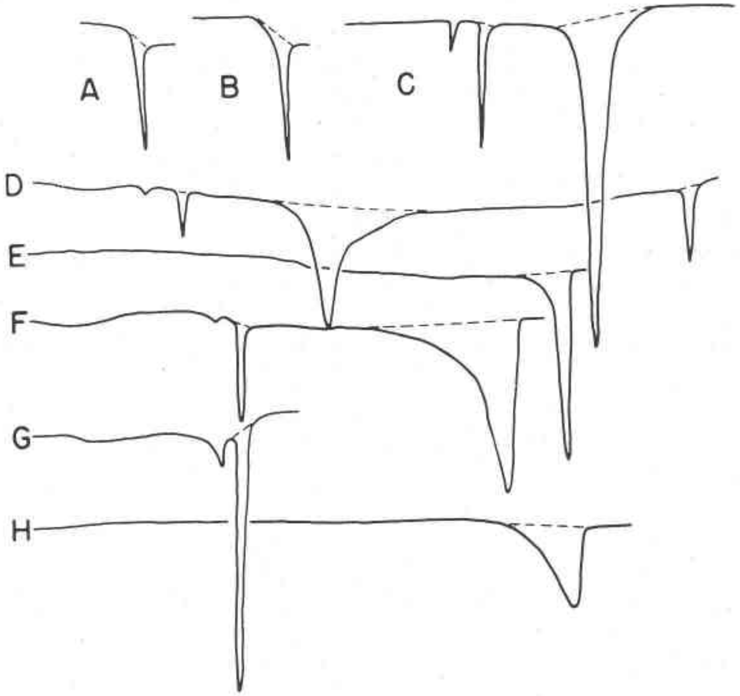

FIG. 10. *D.t.a.* curves of substances useful for the heat of reaction calibration. The substances were dispersed in Al_2O_3 and centered around the thermocouple in a volume of 0.110 c.c. except *B* and *D* which were dispersed in a volume of 0.480 c.c. Rate of heating $=8°$ C. per minute, except $C=12°$ C. per minute.

A. 50 mgm. *m*-dinitrobenzene
B. 100 mgm. benzoic acid
C. 50 mgm. $AgNO_3$
D. 50 mgm. $AgNO_3$
E. 25 mgm. NaCl
F. 15 mgm. $NaNO_3$
G. 50 mgm. $NaNO_3$
H. 10 mgm. $CaCO_3$

can be calculated from heats of formation and heat capacity of the reactants and products (7, 8, 9). The values thus determined are shown in Tables 4 and 5. It is seen that they are in excellent agreement with the calculated values. This excellent agreement verifies not only the accuracy of the scale but also the validity of the derivation relating the proportionality between the peak area of a break in a *d.t.a.* curve and the heat of reaction.

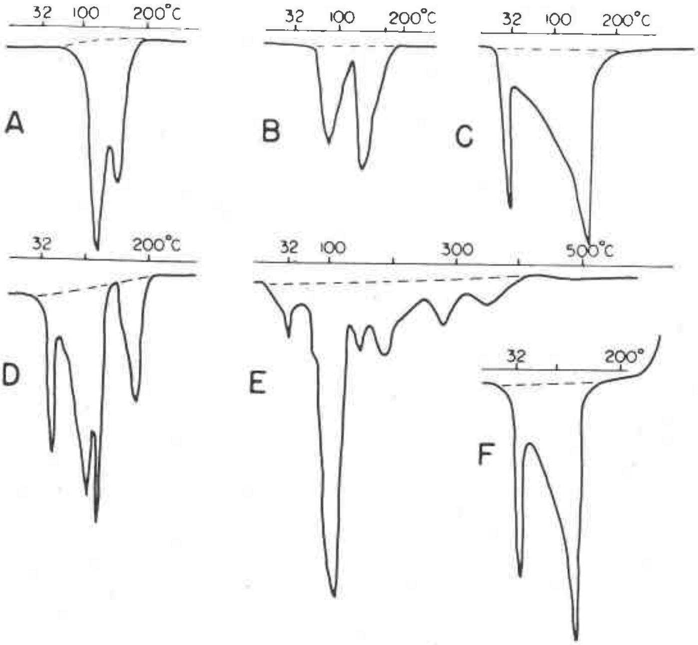

FIG. 11. *D.t.a.* curves of 50 mgm. of various hydrated salts dispersed in Al_2O_3 and centered around the thermocouple in a volume of 0.110 cc.

A. $CaSO_4 \cdot 2H_2O$
B. $BaCl_2 \cdot 2H_2O$
C. $CaNO_3 \cdot 5H_2O$
D. $SrCl_2 \cdot 6H_2O$
E. $MgSO_4 \cdot 7H_2O$
F. $Na_2S_2O_3 \cdot 5H_2O$

A comparison of the shape of the thermal breaks obtained for the various kinds of reactions (Figs. 10, 11) suggests that the desorption of water from gypsum ($CaSO_4 \cdot 2H_2O$), the decomposition of $AgNO_3$ and $CaCO_3$ could be used for a heat of reaction calibration. In fact for the calibration of many instruments, these substances may prove preferable to those previously suggested; for they yield much larger thermal breaks and therefore they are subject to a greater degree of accuracy in measurement. Wittels already suggested for this purpose the use of $CaCO_3$ but the value for the heat of decomposition to which he refers is in error by about

15 per cent. The error appears to be due to failure in correcting the heat of decomposition for the temperature at which it occurs in *d.t.a.*

The method and substances for the heat of reaction calibration for endothermic reactions may also be used for exothermic reactions by merely switching leads to the galvanometer.

DISCUSSION

The value of the suggested method of temperature calibration lies in that the temperature scale reflects all of the heating characteristics inherent in the *d.t.a.* apparatus at the position of the test sample; and that it simplifies the apparatus by eliminating the temperature thermocouple and the associated temperature recording device. Such a simplification would reduce considerably the cost of the apparatus.

The method of registering the temperature scale directly on any *d.t.a.* curve makes possible a precise delineation of the beginning, the peak, and the end of any thermal break. By this method it was shown that the rate of heating apparently has no effect on the initial position of the thermal breaks in *d.t.a* curves of montmorillonite, chlorite, and kaolinite. The differences in position of the breaks in the *d.t.a* curves of these minerals reported in the literature may be due in part to inaccurate temperature scales.

A heat of reaction calibration of the *d.t.a* apparatus in terms of calories per unit peak area would enable the assignment of constant parameter to thermal breaks in *d.t.a* curves of pure minerals. Consequently, it would become possible to compare *d.t.a.* curves of the same mineral or of different minerals obtained with different instruments. Although differences may still appear in *d.t.a.* curves of the same mineral species obtained with different instruments, the difference may reflect differences in the nature of the minerals themselves—such as amount and nature of impurities present, variation in particle size and degree of perfection in crystallization, or other differences.

In reactions involving the liberation of water or CO_2, the heat of reaction may be expressed in calories per unit mass of material being heated and in calories per unit mass of water or CO_2 liberated. The latter expression, however, can be made only when the amount of water or CO_2 liberated during the reaction is known. The magnitude of the heat of reaction as expressed by the first method depends on the purity of the mineral analyzed but by the second method it is independent of the purity. The latter expression for the heat of reaction is, therefore, a better measure for differentiating minerals with overlapping thermal breaks as those of illite and kaolinite in the temperature range between 400° C. and 600° C. In illite the magnitude of the reaction represented by this thermal break is equal to 1025 calories per gram of water liberated whereas in kaolinite it is equal to 1983 calories per gram of water liberated. Several such measurements for various minerals are given in Table 6.

The heat of reaction calibration was found particularly useful in measuring the heats involved in the desorption of water and other liquids from montmorillonite and vermiculite (2). Examples of such measurements are shown in Table 7.

TABLE 6. HEAT OF DECOMPOSITION OF SEVERAL MINERALS AS DETERMINED BY *d.t.a.*

Minerals	Decomposition temperature in *d.t.a.*	Crystal lattice $H_2O(OH)$	Heat of decomposition	
	°C.	per cent*	Cal./gm. of mineral	Cal./gm. H_2O lost
Brucite	356–455	30.92	332	1075
Gibbsite	258–360	31.10	259	832
Goethite	314–396	11.27	105	932
Kaolinite	455–642	12.76	253	1983
Halloysite	430–550	12.00	166	1385
Ca-Montmorillonite	554–723 816–908	2.43 0.70	67 26	2760 3720
Mg-Illite	400–695 790–950	6.25 1.27	64 15	1025 1180

* Of air dry material.

For a heat of reaction measurement to have thermodynamic significance the temperature at which the measurement is made must be stated. Since the temperature increases continuously in *d.t.a.* a heat of reaction measurement applies to a reaction occurring over a wide range of temperature. However, a single temperature point may be assigned to such a reaction by defining such a temperature point as one at which the heat of reaction is equal to that found in *d.t.a.* For convenience sake such a temperature point is designated as t_2 .For the reactions involved in dehydration of crystal lattice water and decomposition of $AgNO_3$ or $CaCO_3$, temperature t_2 may be chosen arbitrarily as the point approximately midway between the beginning and the end temperatures of the

TABLE 7. INTEGRAL HEATS OF DESORPTION OF ADSORBED WATER OF VERMICULITES AND MONTMORILLONITES AS DETERMINED BY *d.t.a.*

Mineral	Adsorbed water	Desorption temperature in *d.t.a.*	Integral heat of desorption	Mean integral heat of desorption
	per cent*	°C.	Cal./gm. of mineral	Cal./gm. H_2O desorption
Mg-Vermiculite	12.7	25–170	130	1026
Mg-Vermiculite	2.7	170–250	38	1415
Ca-Vermiculite	12.4	25–150	113	914
Ca-Vermiculite	3.7	150–210	44	1185
Na-Vermiculite	12.7	25–170	99	779
Mg-Montmorillonite	17.0	25–220	135	794
Ca-Montmorillonite	17.7	25–220	127	718

* Of air dry material.

thermal break representing these reactions. But in reactions involving water desorption, t_2 may be evaluated more accurately by determining the water loss at several of the temperatures at which water loss occurs in *d.t.a.*[1] Subsequently each water loss determination is expressed as a fraction of the total amount of water lost, and multiplied by the rise in temperature to the point of desorption. The sum of these products when added to the initial temperature of the *d.t.a.* apparatus yields temperature t_2 (Table 8). A similar procedure may be followed for evaluating t_2 for the reactions involving loss of crystal lattice water and CO_2 from carbonates.

A clearer concept of the nature of the heat quantities involved in desorption of water from a "wet" mineral may be obtained by picturing the reaction of desorption, namely,

(I) $\text{Mineral}_{\text{(expanded)}} \cdot nH_2O_{(l)\,t1} + \Delta H \rightarrow \text{Mineral}_{\text{(contracted)}\ t2} + nH_2O_{(g)\,t2}$

as if it occurs in the following three steps:

1. The rise in temperature of the "wet" mineral from temperature t_1 to temperature t_2 at which desorption takes place:

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[1] The most accurate method for determining such water losses would be with a *d.t.a.* apparatus so designed that the water loss may be determined at any point during *d.t.a.* In the absence, however, of such instrumentation, water loss from the test sample must be determined in a regulated furnace under conditions of temperature and heating time simulating those of *d.t.a.*

(II) $\text{Mineral}_{\text{(expanded)}} \cdot n\text{H}_2\text{O}_{(l)\,t1} + \Delta\text{H}' \rightarrow \text{Mineral}_{\text{(expanded)}} \cdot n\text{H}_2\text{O}_{(l)\,t2}$

2. The desorption of the water as "liquid" water (l) accompanied by changes in the mineral itself:

(III) $\text{Mineral}_{\text{(expanded)}} \cdot n\text{H}_2\text{O}_{(l)\,t2} + \Delta\text{H}'' \rightarrow \text{Mineral}_{\text{(contracted)}\ t2} + n\text{H}_2\text{O}_{(l)\,t2}$

3. The conversion of the "liquid" water to "gaseous" water at t_2:

(IV) $n\text{H}_2\text{O}_{(l)\,t2} + \Delta\text{H}''' \rightarrow n\text{H}_2\text{O}_{(g)\,t2}$

The heat quantity involved in reaction (I)—ΔH—is termed here *the integral heat of desorption in d.t.a.*

The sum of the heat quantities involved in reactions (III) and (IV) —$\Delta\text{H}'' + \Delta\text{H}'''$—*is termed here the integral heat of desorption at* t_2.

The heat quantity involved in reaction (III)—$\Delta\text{H}''$—is termed here the *integral net heat of desorption at* t_2.

The evaluation of these three heat quantities is as follows:

The *integral heat of desorption in d.t.a.* is determined directly from the peak area in the *d.t.a.* curves and from the analysis of the total loss in water responsible for the peak area.

The *integral heat of desorption at* t_2 is determined by subtracting from the *integral heat of desorption in d.t.a* the heat quantity involved in reaction (II)—$\Delta\text{H}'$. $\Delta\text{H}'$ is evaluated by accounting for the difference in the specific heat of the "wet" and the "dry" forms of the mineral and by a rise in temperature from t_1 to t_2. If we assume that the difference in specific heat between the "wet" mineral and the reference material is equal to the specific heat of the adsorbed water, which in turn is assumed to be equal to the specific heat of liquid water, $\Delta\text{H}'$ would then be equal to the specific heat of water multiplied by the rise in temperature from t_1 to t_2. It was shown previously how to determine t_2.

The absence of an endothermic break prior to the actual desorption reaction itself as in the *d.t.a.* curves of some minerals and some hydrated salts—would indicate that there is no difference in the specific heat between the reference—inert-material and the test sample. $\Delta\text{H}'$ for such desorption reactions would therefore be equal to zero and consequently the *integral heat of desorption at* t_2 would equal the *integral heat of desorption in d.t.a.* The good agreement between the determined and the calculated *integral heats of desorption at* t_2 for several of the salts studied (Table 5) indicates that equating $\Delta\text{H}'$ to zero is permissible.

The *integral net heat of desorption at* t_2 is evaluated by subtracting from the *integral heat of desorption at* t_2 the heat of vaporization of water at t_2.

The three heat quantities may be expressed as calories per gram of material undergoing desorption and as calories per gram or mole of water being desorpt. The latter expression is obtained by dividing the former one by the amount of water liberated from 1 gram of material and multiplying by 1 or 18.

To evaluate the heat quantities involved in desorption at temperatures other than t_2, the effect of temperature on the reaction of desorption must be estimated. The method of estimating this effect is the same as for any other reaction and the procedure followed is the one given by Lewis and Randall (9). The method mainly accounts for the difference in the heat capacities or specific heats at constant pressure between the reactants and products which is designated as ΔC_p.

Since the *integral heat of desorption at* t_2 is the sum of the heats involved in reactions (III) and (IV), it would be simpler to evaluate separately the effect of temperature on each of these reactions.

In reaction (III), which involves *the integral net heat of desorption*, ΔC_p

Table 8. Calculation of the Heat Quantities Involved in Vaporization of One Gram of Water from Utah Ca-Montmorillonite under Conditions Similar to those Existing during *d.t.a.*

Column number						
1	2	3	2×3	4	3×4	2×3+3×4
Temperature at point of desorption	Temperature* rise to point of desorption	Fraction of total desorpt† water	Heat absorbed by fraction during rise in temperature	Heat of vaporization	Heat absorbed by fraction during vaporization	Total heat absorbed by fraction
°C.	°C.	gm.	cal.	cal./gm.	cal.	cal.
75	50	0.69	34.5	554.3	382.3	416.8
100	75	0.13	9.8	539.0	70.0	79.8
115	90	0.04	3.6	529.3	21.2	24.8
145	120	0.10	12.0	508.3	50.8	62.8
230	205	0.04	8.2	423.3	17.3	25.5
Totals		1.00	68.1		541.6	609.9

* Temperature rise was computed from an initial temperature of 25° C.

† Total desorpt water = 19.0 gms. per 100 gms. air dry clay.

1. Temperature t_2 is equal to the total of column 2×3—namely, 68.1 plus 25° C., the initial temperature, or 93.1° C.
2. *Integral heat of desorption in d.t.a. was determined* to be equal to 143.5 cal. per gm. air dry clay or 143.5×1/0.19 = 754 cal. per gm. of water desorpt.
3. Integral heat of desorption at t_2—assuming that the difference in the specific heat between "wet" and "dry" clay is equal to that of water—= 143.5 − 68.1×0.19 = 130.5 cal. per gm. air dry clay, or 130.5×1/0.19 = 686 cal. per gm. of water desorpt.
4. Integral heat of desorption at 25° C. = 130.5 + (583 − 542)×0.19 = 137.8 cal. per gm. air dry clay or 137.7×1/0.19 = 726 cal. per gm. of water desorpt (583 = heat of vaporization at 25° C., 542 = heat of vaporization at 93° C.).
5. *Integral net heat of desorption* = 130.5 − 542×0.19 = 27.5 cal./gm. air dry clay or 27.5×1/0.19 = 145 cal. per gm. of water desorpt.

is equal to the difference in the heat capacities of the "wet" mineral and that of the "dry" mineral and liquid water. If we assume that the difference in the heat capacities of the "wet" mineral and the "dry" mineral were equal to that of liquid water, ΔC_p in reaction (III) would then be equal to zero. In consequence the *integral net heat of desorption* would be independent of temperature.

Since reaction (IV) represents the evaporization of liquid water, the effect of temperature on this reaction may be found directly in standard steam tables which list the heat of vaporization at different temperatures. The effect of temperature may also be calculated from the difference in the heat capacity of liquid water and gaseous water and one known heat of vaporization at a known temperature.

It appears, therefore, that the effect of temperature in *d.t.a.* on the *integral heat of desorption* is identical to the effect of temperature on the heat of vaporization of water. The difference in the *integral heat of desorption* at two temperatures is, therefore, equal to the difference in the heat of vaporization of water at the two temperatures.

The data of Table 8 illustrates the method of evaluating temperature t_2, the *integral heat of desorption at* t_2 *and* t_1, and the *integral net heat of desorption* for a Utah Ca-montmorillonite having a water content of 19.0 gm. per 100 g. air dry clay.

The proposed method for evaluating *the integral heat of desorption* and *the integral net heat of desorption* for adsorbed water is also applicable to other adsorbed liquids. Moreover these heat quantities would be equal but opposite in sign to the heat quantities involved in sorption reactions, provided the sorption and the desorption reactions are completely reversible, that is, without hysteresis.

Conclusions and Summary

(1) A uniform rise in temperature in the sample holes containing the differential thermocouples enables a simultaneous *d.t.a.* of several substances each of which marks a fixed temperature reference point in the resulting curve. Such a curve yields directly the temperature scale. To accomplish the analysis small amounts (2 to 10 mgm.) of the desired substances are placed either in one or in both of the sample holes around the thermocouple. To prevent the substances from interacting with each other they are embedded between narrow layers of Al_2O_3. A list of substances found useful for this purpose is given and they are termed "temperature indicators."

(2) By placing small amounts of the desired temperature indicators above and below a test sample or with the reference material, the temperature scale may be registered directly on the *d.t.a.* of the test sample. Several such *d.t.a.* curve are shown.

(3) Two methods are given for determining the sensitivity of the *d.t.a.* apparatus at different temperatures: one involves the use of temperature indicators and the other involves the use of boiling water and the tables of thermocouple characteristics.

(4) The intensity of a thermographic response, as measured by the peak height and peak area, to a thermal reaction in a given mass of material was found to be inversely proportional to the distance of the material from the thermocouple and to the volume which it occupies when centered around the thermocouple.

(5) The relation between the intensity of the thermographic response and the thermal reaction occurring in different amounts of the same material when dispersed in an identical volume and centered around the thermocouple was found to be linear.

(6) Organic substances of known heats of fusion and hydrated salts, particularly gypsum, of known heats of desorption were found useful for the heat of reaction calibration below 200° C., whereas inorganic substances of known heats of fusion or decomposition for the heat of reaction calibration above 200° C. Among the latter substances $AgNO_3$, $NaNO_3$ and $CaCO_3$ proved particularly useful.

(7) In determining in an unknown sample a heat of reaction or an amount of a known mineral, the sample should be confined to the same volume and placed in the same position with respect to the thermocouple as the substances used for calibration.

(8) Excellent agreement between determined and known heats of reaction of several substances attested to the accuracy of the heat of reaction scale and also to the validity of the proportionality between the peak area of a thermal break of a *d.t.a.* curve and the heat of reaction responsible for the break.

(9) Ascertaining the temperature scale of the *d.t.a.* apparatus by using the differential thermocouple circuit enables a simplification of the apparatus and thereby also a reduction in its cost.

(10) A heat of reaction calibration enables the assignment of constant parameters to *d.t.a.* curves of pure minerals and consequently *d.t.a.* curves obtained with different instruments become comparable.

(11) One of the most useful applications for the heat of reaction calibration was found in measuring the heat quantities involved in water desorption of hydrated minerals.

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