ABSTRACT

THE MEASUREMENT OF HEATS OF REACTIONS OF SOIL COMPONENTS WITH A DIFFERENTIAL THERMAL ANALYSIS APPARATUS

by Boyd Gene Ellis

The differential thermal analysis apparatus was used to measure heats of desorption of NH_3, methylamine, and ethylamine from clay minerals.

A theoretical discussion of the nature of heat flow within a differential thermal analysis sample holder was presented. The conclusions drawn from the theoretical discussion were related to the calibration curve of the heat of reaction versus area under the differential thermal curve made using nine different salts of known heats of inversion or fusion.

Two methods of determination of heats of reaction by use of differential thermal analysis were compared. The heats of decomposition of magnesite and dehydroxylation of kaolinite determined by use of the Clausius-Clapeyron equation and the standard curve prepared by using pure salts deviated less than four per cent.

It was shown that the exothermic reaction observed upon release of NH_3 from bentonite clay is due to oxidation of the NH_3 catalyzed by the platinum thermocouples. A method was perfected using nitrogen gas to eliminate oxidation during analysis. Losses of both water and NH_3, methylamine, or ethylamine occurred between 200 and 550 degrees centigrade. It was postulated that the water loss between 200 and 450 degrees centigrade evolves from decomposition

of $Al(OH)_3$. The average heat of desorption for the simultaneous loss of one mole of NH_3 and one mole of water between the temperatures of 200 and 450 degrees centigrade was 35.3 kilocalories. The average heat of desorption for methylamine under similar conditions was found to be 40.9 kilocalories. The desorption of ethylamine was accompanied by losses of large quantities of water; consequently, no heats of desorption could be directly connected with loss of ethylamine.

Studies conducted with formic acid, acetic acid, methanol, and ethanol saturated bentonite indicated that small quantities are retained by the bentonite, but that the bonding energies are not measurable by differential thermal analysis.

Accurate quantitative studies were not possible with the vermiculite used because the thermal properties of the sample changed upon heating.

It was shown that the method of eliminating oxidation with nitrogen gas during differential thermal analysis could be applied to soils high in organic matter yielding differential thermal analyses curves characteristic of the mineral components of the soils.

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A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Soil Science

1961

ACKNOWLEDGMENTS

This author wishes to express his sincere gratitude to Dr. Max M. Mortland for his guidance, suggestions, and especially for his willingness to discuss any and all points of interest which arose during the research conducted in this thesis and other research work encountered during the course of study at Michigan State University. His interest and enthusiasm in fundamental research has been an inspiration.

Special thanks goes to my wife, Julia, for the many hours she spent tracing differential thermal analyses curves and the tedious task of cutting out the areas enclosed by the curves.

This author would also like to thank the members of his guidance committee for their helpful suggestions concerning the course work program and research program.

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CHAPTER I

INTRODUCTION

One of the major aims of science in fundamental research is to isolate, identify, and understand the individual steps occurring in a reaction. Soil science presents a special problem in conducting fundamental research. Soils, as they occur in nature, are very complex. Thus, a variety of soil components may be selected for study.

The more inert components are generally found in the sand and silt fractions of the soil. As the particle size is reduced, the specific surface becomes much greater, thereby yielding more highly reactive particles. Mortland and Kemper (20) have suggested that such important properties as water retention and cation exchange capacity are highly correlated with surface area of soils. Since the more reactive portion of the soil is found in the clay and organic fractions, it appears that these should be of primary interest to the soil scientist. However, in the study of these fractions many complex situations arise. Soil organic matter which is resistant to further decay, called humus, is far from consistent in chemical composition or reaction. For example, McGeorge (17) and Turner (34) have reported values for the cation exchange capacity of soil organic matter ranging from 150 to 250 milliequivalents per 100 grams of humus while Olson and Bray (23) working with other

American soils have reported values ranging from 30 to 280 milliequivalents per 100 grams of humus. According to Van der Marel (35) even kaolinite from pure, well known deposits have heats of transformation which vary from 100 to 176 and from 23 to 43 calories per gram for their endothermal (600° C) and exothermal reactions (980° C) respectively.

Thus, to study such a complex system as the soil one must draw on special research tools and many times revert to pure systems to gain insight to the fundamental reactions occurring in various soils. The research tool utilized in this study was differential thermal analysis.

Differential thermal analysis has been utilized by investigators studying soil components as early as 1887 when Le Châtelier (14) employed a simple apparatus to measure thermal reactions taking place when clay materials were heated. In 1899 Roberts-Austen (24) initiated the forerunner of the modern day differential thermal apparatus in which the temperature differences are measured between a material being studied and a reference material. An examination of the theory underlying the electromotive force arising from a thermocouple shows that a net electromotive force will only be developed when the reference material is at a different temperature than the material being studied. Thus, any change in state during heating of the material which is accompanied by a change in heat content will produce an electromotive force. Since many soil components have characteristic reactions during heating, differential thermal analysis has been utilized for many years in qualitative estimation of soil components. An excellent review of the literature concerning identification of clay minerals by differential thermal analysis is given by Grim (10).

Since the magnitude of the electromotive force produced is proportional to the net difference in temperature between sample and reference material, differential thermal analysis should be a quantitative measure of the heat changes during a run. Following this trend of thought several investigators, Norton (22), Kiyoura and Sata (13), Murray, et al. (21), and Grimshaw and Roberts (11), have attempted to utilize differential thermal analysis as a rapid, inexpensive, and accurate method for quantitative determinations of clay minerals. Considerable difference of opinion has been expressed about the reliability of differential thermal analysis for quantitative determinations. Speil (28) found deviations of about 30 per cent in heats of transformation of kaolinite from various locations. The limitations for quantitative determinations of clay minerals by differential thermal analysis has been thoroughly discussed by Van der Marel (35). From his discussion it appears that the basic limitation is with the variations in the naturally occurring clay minerals and not with the instrument. However, since the measurements made by differential thermal analysis are of heats of reaction occurring when a sample is heated at a constant rate, several factors inherent with the instrument tend to limit its use as a quantitative instrument. According to Barshad (3) 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 analyses curves on the heat of reaction of the sample has been derived theoretically by several investigators (28), (29), (12), (7), (8), (9). This method has been applied by Barshad (3) in measurement of heat of inversion and melting of several pure compounds and also to dehydration of certain clay minerals. On the other hand, Stone (31), utilizing a variable pressure apparatus, has applied the Clausius-Clapeyron equation for determination of heats of dehydration and decomposition of clay minerals and magnesite.

The object of this thesis is to (1) examine the differential thermal analysis apparatus as an instrument for the determinations of heat of reaction involving clay minerals, (2) compare two methods of determining the heat of reaction utilizing differential thermal analysis, and (3) evaluate the heats of reaction of ammonia and simple organic materials in combination with pure clay minerals. It is hoped that a study of pure systems will yield a greater insight to studies made on soil systems with differential thermal analysis and to bonding energies of various clay-ammonia and clay-organic combinations.

CHAPTER II

MEASUREMENT OF ENTHALPY BY DIFFERENTIAL THERMAL ANALYSIS

For a complete understanding of measurement and interpretation of any thermodynamic quantity the basic principles underlying its origin must be examined.

Enthalpy, sometimes called heat content, is defined as

$$H = E + PV \tag{1}$$

where E is internal energy, P is pressure, and V is the volume of the system. It is worthy to note that enthalpy is a property of the state of the system since each of the right hand terms of the defining equation is a state function. Since by classical thermodynamics, E, the internal energy of a system, may not be measured in absolute magnitude, enthalpy also may not be measured in absolute magnitude and only measurements of changes in enthalpy, generally referred to as ΔH, may be made.

The relationship between change in enthalpy and heat evolved during a reaction may be obtained as given below. By the definition given in equation (1), $H = E + PV$. Differentiation yields

$$dH = dE + PdV + VdP. \tag{2}$$

But from the first law of thermodynamics $dE = đQ - đW$; therefore,

$$dH = đQ - đW + PdV + VdP. \tag{3}$$

Equation (3) may be simplified greatly if measurements are restricted to systems at constant applied pressure in which there is only pressure-volume work being accomplished. In this restricted system VdP ≅ 0 and dW = PdV, thus yielding

$$(dH)_P = (dQ)_P. \tag{4}$$

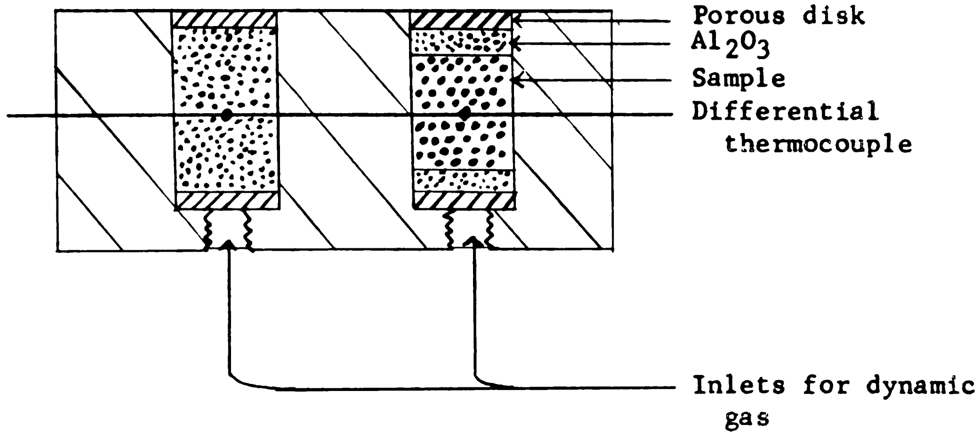
Therefore, a measure of the heat changes involved in a reaction occurring at constant pressure with only pressure-volume work will yield the change in heat content directly.

With a differential thermal analysis apparatus the measurement of the heat changes during a reaction is complicated by the fact that heat is being added to the system and the temperature of the system is being increased during a determination. The problem of obtaining the heat of reaction from differential thermal analysis data was approached from a theoretical point of view by Speil (28). Kerr and Kulp (12) made certain modifications and corrections of the original derivation by Speil. Eriksson (7) suggested that both the derivation and modifications are too simplified to be useful. One approach utilized by Eriksson (9) has been adapted to the boundary conditions of the particular differential thermal apparatus used in this study and is given below.

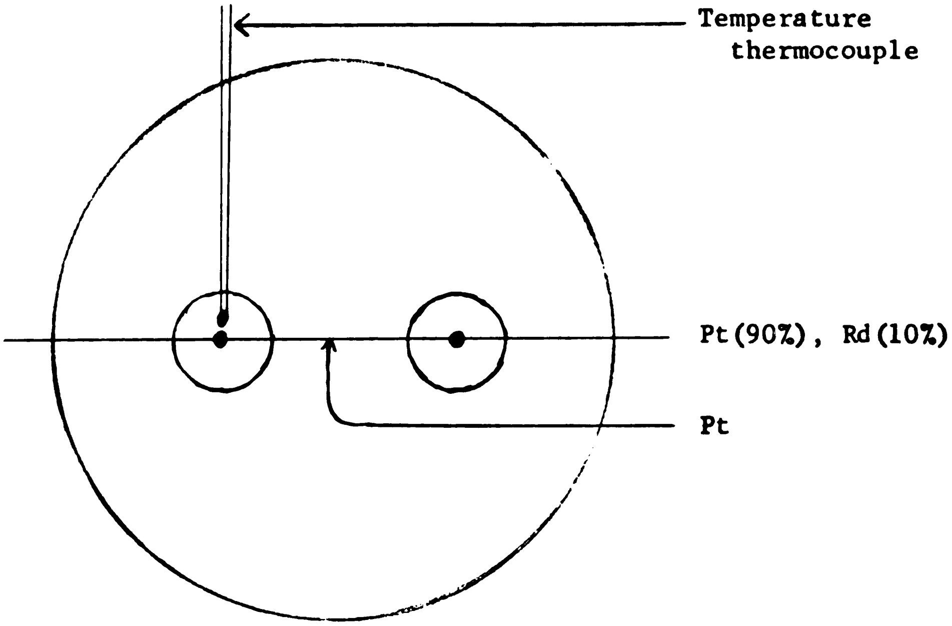
Considering the reference space, see figure 1, the differential equation for heat flow within that space may be given as follows:

$$\frac{A(t)}{K} + \nabla^2 T_r = \frac{1}{\alpha_r^2}\frac{\partial T_r}{\partial t} \tag{5}$$

where A(t) is the external heat being added which is a function of time, K is the heat conductivity, ∇^2 is the Laplacian operator, T_r is the temperature of the reference material, α_r^2 is the diffusivity, and



Cross Sectional View



Top View

Figure 1. Diagram of the differential thermal analysis sample holder; twice actual size.

t is time. The differential equation for the sample space will be similar except a term must be added to account for the production or absorption of heat by the sample. Therefore, the following differential equation is written for the sample space,

$$\frac{A(t)}{K} + \frac{B}{K}\left[T_s, \left(\frac{\partial T_s}{\partial t}\right)\right] + \nabla^2 T_s = \frac{1}{\alpha_s^2}\frac{\partial T_s}{\partial t} \tag{6}$$

where T_s is the temperature of the sample and $B\left[T_s, \left(\frac{\partial T_s}{\partial t}\right)\right]$ is the heat produced or absorbed by the sample.

If equation (5) is subtracted from equation (6) and W is substituted for $T_s - T_r$, the result is

$$\nabla^2 W + \frac{B}{K}\left[T_s, \left(\frac{\partial T_s}{\partial t}\right)\right] = \frac{1}{\alpha_s^2}\frac{\partial T_s}{\partial t} - \frac{1}{\alpha_r}\frac{\partial T_r}{\partial t}\,. \tag{7}$$

By multiplying both sides of equation (7) by dt and integrating between the limits of t_1 and t_2, where t_1 is some time before any reaction has occurred in the sample space and t_2 is a time after a reaction has occurred in the sample space and T_s again equals T_r, the equation obtained is

$$\int_{t_1}^{t_2}\frac{\partial^2 W}{\partial x^2}dt + \int_{t_1}^{t_2}\frac{\partial^2 W}{\partial y^2}dt + \int_{t_1}^{t_2}\frac{\partial^2 W}{\partial z^2}dt + \frac{Q}{K} = \left(\frac{T_s}{\alpha_s^2} - \frac{T_r}{\alpha_r^2}\right)\Bigg|_{t_1}^{t_2}. \tag{8}$$

But the bounded area, S, recorded is

$$S = K'\int_{t_1}^{t_2} W\,dt\,; \tag{9}$$

therefore, equation (9) may be rewritten to yield

$$K'\nabla^2 S + \frac{Q}{K} = \left(\frac{T_s}{\alpha_s^2} - \frac{T_r}{\alpha_r^2}\right)\Bigg|_{t_1}^{t_2}. \tag{10}$$

In many cases the diffusivity of the sample may approach the diffusivity of the reference material. For example, if the sample to be run is diluted with the reference material and similar packing utilized in both the reference and the sample space, α_s^2 should approach α_r^2. Evidence will be given later which indicates that with bentonite and Al_2O_3 α_s^2 approaches α_r^2. If $\alpha_s^2 = \alpha_r^2$, the right hand term of equation (10) becomes zero yielding the Poission Equation given as equation (11),

$$\nabla^2 S = -\frac{Q}{k'K}. \tag{11}$$

If cylindrical sample holders are used, it is much more convenient to express equation (11) in cylindrical polar coordinates. Thus,

$$\frac{\partial^2 S}{\partial r^2} + \frac{1}{r}\frac{\partial S}{\partial r} + \frac{1}{r^2}\frac{\partial^2 S}{\partial \varphi^2} + \frac{\partial^2 S}{\partial z^2} = -\frac{Q}{k'K}. \tag{12}$$

If the thermocouple is centered in the sample holder ($r = 0$, $z = 0$), it is obvious that $\frac{\partial S}{\partial \varphi} = 0$. If the assumption is made that the heat conductivity of the metal block is much greater than the heat conductivity of the sample, the temperature of the block may be assumed to be constant throughout. Thus, the principal addition of heat will be from the cylinder wall surrounding the sample. It may further be observed from figure 1 that heat production should be uniform with respect to the z axis. Thus, the principal heat gradient and heat flow for the particular apparatus described should be along planes of $z = k$. Further evidence of the validity of this assumption has been given by Barshad (3). He 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 planes of $z = k$ even when a vertical heat gradient exists. Therefore, when the vertical heat gradient is very small and particularly small in the region of the thermocouple, a reasonable assumption is that $\frac{\partial S}{\partial z}$ approaches zero. This yields the more restricted differential equation

$$\frac{\partial^2 S}{\partial r^2} + \frac{1}{r}\frac{\partial S}{\partial r} = -\frac{Q}{k'K}. \tag{13}$$

A particular solution of this differential equation is

$$S = -\frac{Q}{4K'K} r^2 + C . \tag{14}$$

Since the temperature of the block is assumed to be constant throughout, the boundary condition that $S = 0$ for $r = a$, where a is the radius of the holes in the sample holder, must be imposed. This yields the solution

$$S = \frac{Q}{4K'K}(a^2 - r^2). \tag{15}$$

Thus, if the thermocouple is placed at $r = 0$, $z = 0$, the area recorded should be a linear function of the quantity of heat evolved or absorbed by the sample during a given run.

Many attempts have been made by various investigators to calibrate the differential thermal analysis apparatus for quantitative measurements. An extensive review of these attempts is given by Smothers and Chiang (26). Many methods have been proposed to select the proper boundaries for the areas recorded. It has been noted that difficulties arise when the base line fails to return to its normal position after a reaction. This condition arises when the heat capacities or the thermal diffusivity of the sample change upon heating or reaction. Examination of the equations for heat flow shows that a change in heat capacities or thermal diffusivity will yield a differential equation whose solution would not be linear. It may also be noted that a calibration with one material may not be applied to other materials in this case unless the circumstance occurs where the changes in heat capacity and thermal diffusivity are the same for the material used in calibration as for the unknown materials. It would appear that care must be exercised in applying quantitative measurements to such systems. One of the first useful calibrations of a differential thermal analysis apparatus was made by Wittels (36). However, his calibrations were made utilizing only one material, $CaCO_3$. As such, its reliability is limited to a narrow range in temperature and materials since he found that the base line did not return to its original position after the decomposition reaction. One of the more extensive empirical studies of the factors affecting the calibration of the differential thermal analysis apparatus was made by Barshad (3). He found that one of the more important factors affecting the peak area was the volume in which the sample was dispersed. As the volume increased from 0.04 to 0.49 cubic centimeters with the amount of kaolinite constant, the peak area decreased from 4.06 to 1.62 square centimeters. However, he found that the peak area per given amount of sample remained constant as long as a constant volume was used. Barshad also stated that the peak area is affected by heating rate. This has been a point of considerable discussion by several investigators. Speil (28) stated that the area of a differential thermal analysis peak should be independent of the heating rate, except for the effect of variation of second order differential quantities with the heating rate. Using Georgia kaolinite he found less than two per cent deviation when the heating rate was changed from 5 to 20 degrees centigrade per minute. Arens (1), studying a variety of clay minerals and quartz, and Wittels (36), studying tremolite, reported rather large effects of heating rate on the peak area. It should be noted from the theoretical derivation presented in this thesis and also those presented by Speil, et al. (29) and Eriksson (9) that if the condition is met that the heat capacities and thermal conductivities of the sample and reference material are the same during the run, the area will be independent of heating rate. As noted before, it is questionable if satisfactory quantitative work with differential thermal analysis can be performed if these conditions are not met. Therefore, the observation of Arens (1) and Wittels (36) that the area was a function of heating rate should have led to the conclusion that for their particular system the peak area was not a linear function of the quantity of heat released. A similar statement could be made concerning Barshad's (3) work; however, he did not present experimental evidence to verify his statement that the heating rate affected the area. Barshad presented data which showed that the electromotive force produced by a Pt - Pt (90%) Rh (10%) thermocouple increases with temperature for a given temperature differential. From his data it appears that this effect is negligible for temperature differences less than 10 degrees centigrade or temperatures above 200 degrees centigrade. Below 200 degrees centigrade the electromotive force decreases for a given temperature difference, even for small temperature differences.

Three methods of calibration of the differential thermal apparatus were investigated during the course of this thesis. The first method attempted was that described by Wittels (36). Amounts of pure salt ranging from 20 to 30 milligrams with known heats of fusion were placed around the thermocouple. The heating rate was maintained at 14 degrees centigrade per minute. This method failed to produce a linear function and was very difficult to reproduce. It is felt that the major difficulty encountered was in reproducing the location of the extremely small sample with respect to the thermocouple.

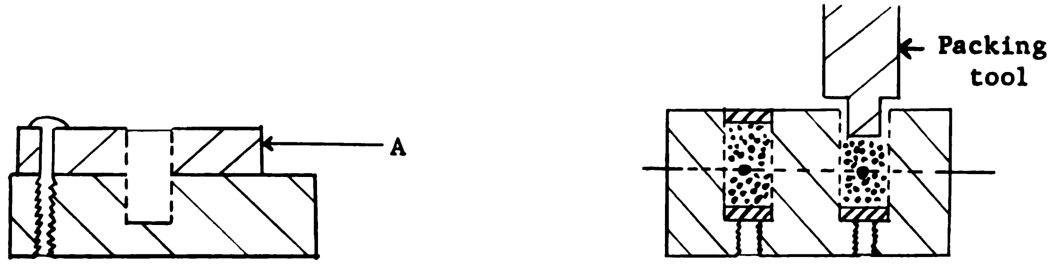
The second method investigated involved preparing samples of pure salts diluted with Al_2O_3. Two hundred fifty milligrams of each sample were packed around the thermocouple before running differential thermal analysis. Although this method had the advantage in that the location of the sample with respect to the thermocouple could be reproduced, the volume occupied by the sample was controlled by the density of the mixture. As Barshad pointed out, the volume occupied by the sample is critical; therefore, as would be expected, this method did not produce a reliable calibration curve. The function was linear where the ratio of salt to Al_2O_3 was small but deviated from a straight line where the ratio of salt to Al_2O_3 was high.

The third method tested was found by this author to be the most successful. It was similar to that suggested by Barshad (3). Table I gives a list of the materials utilized together with the temperature of the reaction, ΔH of reaction, and the range in per cent of the material used. The temperature of reaction and heat of reaction data were obtained from the National Bureau of Standards Circular 500 except for KNO_3. A discrepancy appeared between these tables and the Handbook of Chemistry and Physics for KNO_3. The value used for KNO_3 in this calibration was 2.28 kilocalories per mole as given in the Handbook of Chemistry and Physics. To prepare the standard material a small quantity of the compound 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 with~~ a Wig-L-Bug ~~dental grinder~~ for a period of five minutes. To obtain a constant volume with the same packing each time the sample was packed in a container shown diagramically in figure 2. After packing the sample the part labeled "A" was moved

TABLE I

DATA FOR MATERIALS USED IN CALIBRATION OF DIFFERENTIAL THERMAL ANALYSIS APPARATUS

Material		Type of Reaction	Temperature °C	Δ H K Cal/mole	Range in % Used
M-dinitrobenzene		Fusion	90	4.15	25 - 70
NH_4Cl		Fusion	184	1.00	15 - 50
$AgNO_3$	a.	Transition	160	0.66	4 - 55
	b.	Fusion	210	2.76	
$NaNO_3$	a.	Transition	275	--	4 - 25
	b.	Fusion	310	3.8	
KNO_3	a.	Transition	128	1.30	20 - 50
	b.	Fusion	337	2.28	
Quartz		Transition	573	0.15	100
K_2SO_4		Transition	583	1.94	4 - 55
RbCl		Fusion	717	4.40	5 - 25
NaCl		Fusion	808	6.8	4 - 10



Constant Volume Tool

Sample Holder

Figure 2. Cross sectional diagram of tools used for packing the sample in the sample holder; actual size.

so as to slice the sample at a constant volume. The sample was placed on weighing paper, the exact weight determined, and transferred to the sample hole in the nickel block. Prior to placing the sample in the nickel block 30 milligrams of Al_2O_3 were placed in a thin, even layer in the bottom of the sample hole. To assure that the sample was always packed to the same volume a tool was designed as shown in figure 2. After compressing the sample until the shoulder of the tool reached the nickel block the remaining space was filled with Al_2O_3. The heating rate utilized for this calibration was 13.0 ± 0.5 degrees centigrade per minute. The instrument utilized for this calibration and in all subsequent studies conducted for this thesis was a handmade instrument manufactured by the Robert L. Stone Company, Austin, Texas. The furnace is essentially a cylindrical furnace well insulated from all sides, top, and bottom. The rate of heating is controlled by a rheostat driven by a variable speed motor so that a linear heating rate between 10 and 18 degrees centigrade per minute may be maintained. The differential thermocouple is connected in series with a variable but accurately known resistance to a Leeds and Northrup swing mirror galvanometer. The mirror position is relayed through an optical system to two balanced photoelectric cells in a Beckman Photopen Recorder. In all quantitative work a resistance of 100 ohms in the differential thermocouple circuit was used which gives about three centimeter deflection for an α to β quartz transition. The temperature of the reference material was recorded by a Pt - Pt (90%) Rd (10%) thermocouple in conjunction with a Weston Recorder. The instrument is also equipped to mark the temperature in 100 degree increments on the differential curve. The chart speed for the recording of the differential curve was set at a maximum of two inches per minute. It was felt that greater accuracy of measurement could be obtained if the areas were made as large as possible.

Typical curves for the materials utilized for calibration of the differential thermal analysis apparatus are shown in figure 3. The dotted lines are extensions of the base line which were used to enclose the areas. As can be seen, very little drift was obtained in the base lines except for $NaNO_3$. Even for $NaNO_3$ little difficulty was encountered in establishing where the curve departed from the base line and returned to the base line. The calibration curves obtained are shown in figure 4. Each point on the curve is a mean of two replications. The areas were determined by tracing them on drafting paper and then cutting out the areas and weighing them with an analytical balance. Each area was cut out three times and the mean of the three weights used. Although the curves shown in figure 4 are not strictly linear over the entire region, the points give a well defined function. It should again be pointed out that Barshad's data would predict deviation for reactions that occur below 200 degrees centigrade.

Application of Clausius-Clapeyron Equation

The differential thermal apparatus used in this investigation was equipped to control the atmosphere and the pressure surrounding the sample during a run. This instrument has the further advantage in that the gas introduced to the bottom of the sample may be maintained at a slightly greater pressure than the gas at the top

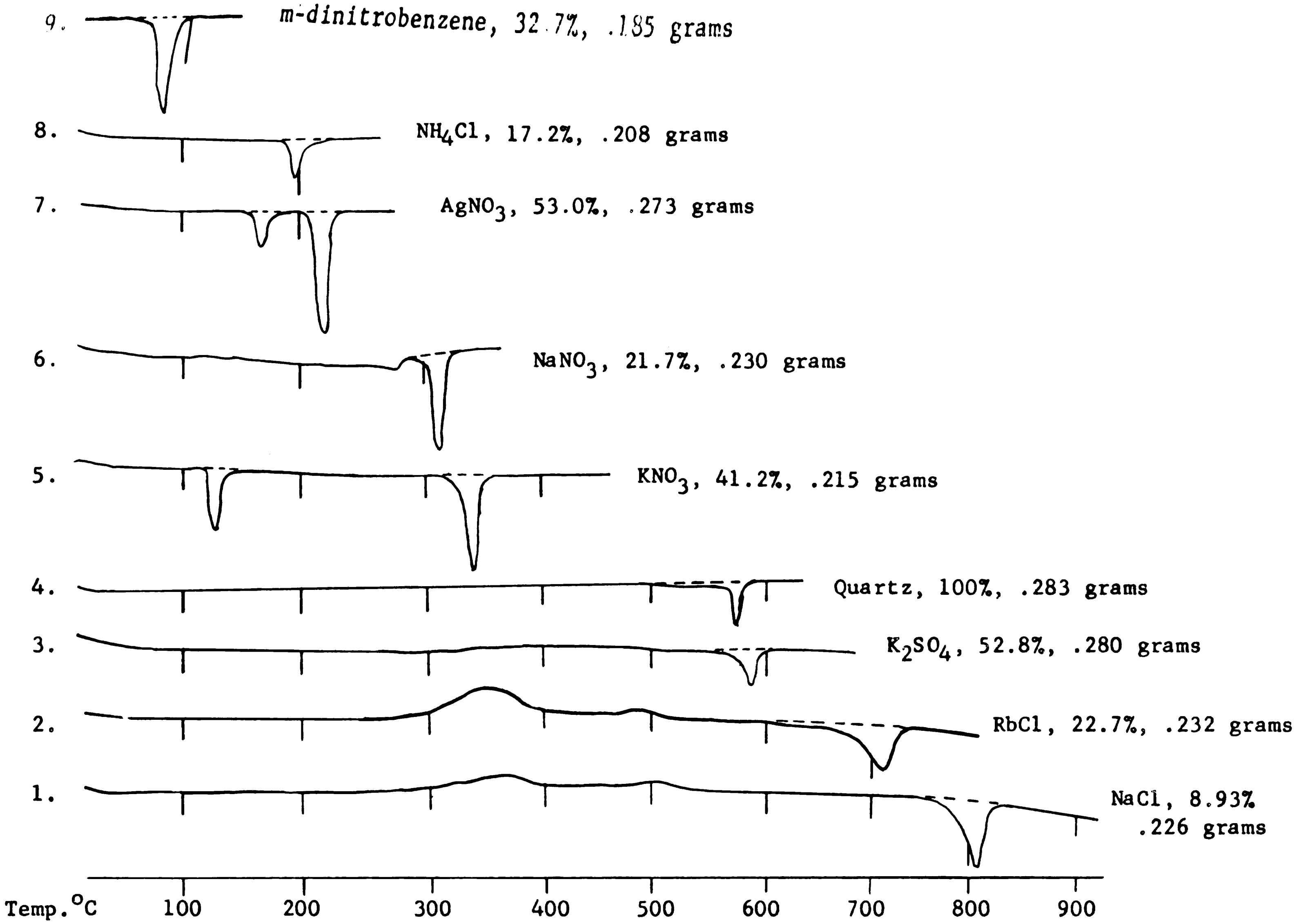


Figure 3. Differential thermal analyses curves of materials used for heat of reaction calibration.

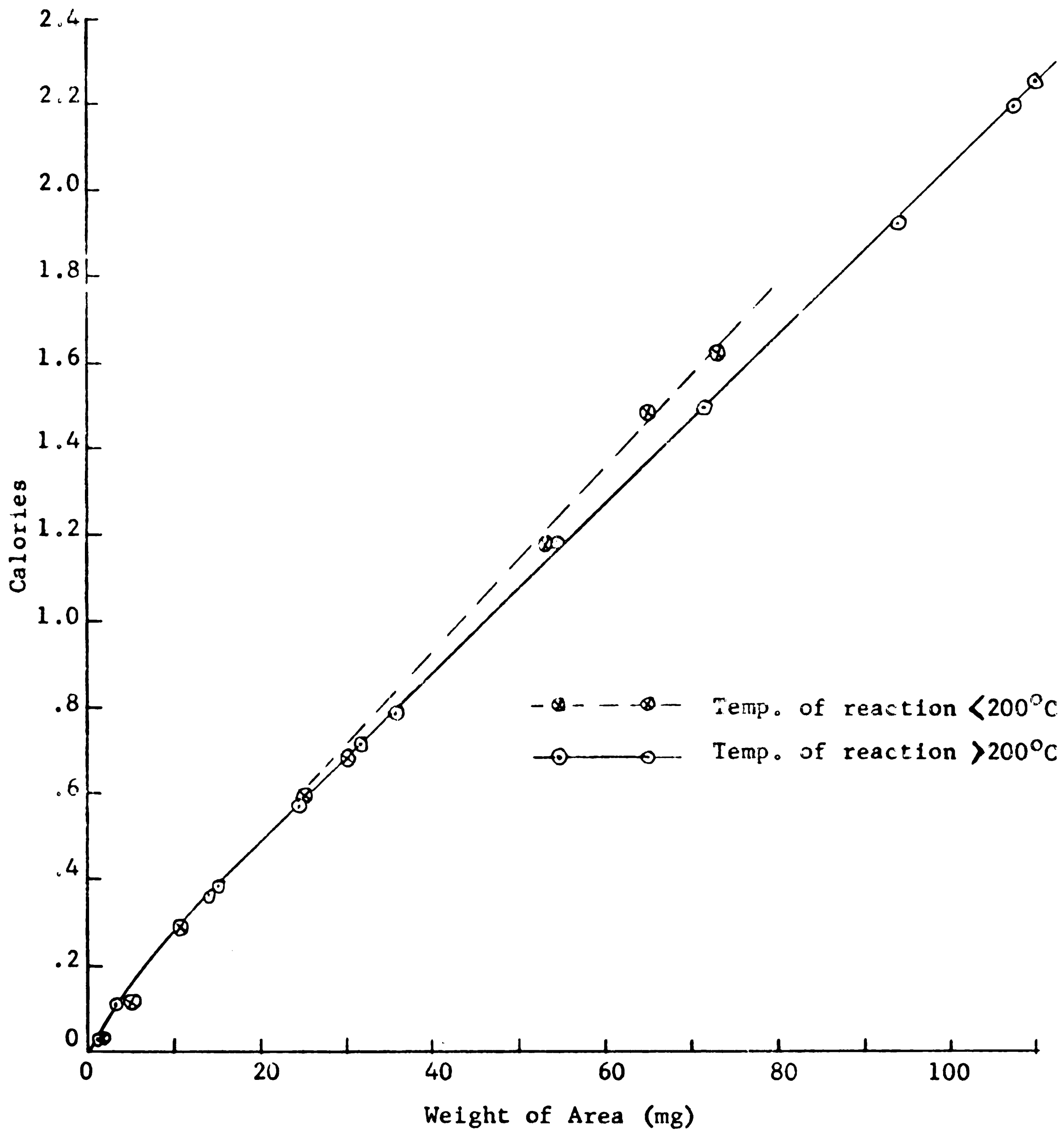


Figure 4. Calibration curve for heat of reaction versus area under the differential thermal analysis curve.

of the sample, thereby producing a flowing or dynamic gas. Thus, it is possible to maintain the gas surrounding the sample at a constant composition during the run despite the decomposition products produced by the sample during the run. A complete description of this arrangement is given by Stone (32). Stone (30) has suggested that this instrument is very useful for determining ΔH of decomposition by use of the Clausius-Clapeyron equation. Before using the Clausius-Clapeyron equation an examination should be made of its origin to determine its applicability and restrictions. The following relationship from the Maxwell equations may be utilized:

$$dF_s = -S_s\,dt + V_s\,dP \tag{16}$$

where F_s is free energy of the solid or liquid, S_s is entropy of the solid or liquid, t is temperature, V_s is volume of solid or liquid, and P is pressure;

$$dF_g = -S_g\,dt + V_g\,dP \tag{17}$$

where F_g is free energy of the gas, S_g is entropy of the gas, and V_g is equal to the volume of the gas. It must be noted, however, that equations (16) and (17) are restricted to a system to which this Maxwell equation applies; namely,

1. Closed system of fixed mass,
2. Single phase,
3. No reaction, and
4. Pressure-volume work only,

or

1. Closed system,
2. Pressure-volume work only, and
3. Reversible reaction.

For a reversible phase transition it is required that $dF_s = dF_g$. Therefore,

$$-S_g\,dt + V_g\,dP = -S_s\,dt + V_s\,dP. \tag{18}$$

Assuming an ideal gas where $V_g = \frac{nRT}{P}$, assuming that $V_g \rangle\rangle\rangle V_s$, and rearranging equation (18) yields

$$(S_g - S_s)\,dt = \frac{nRT}{P}\,dP. \tag{19}$$

For a reversible phase transition $\Delta S = \frac{\Delta H}{T}$.. Therefore,

$$\frac{\Delta H}{nR} \cdot \frac{dT}{T^2} = \frac{dP}{P} \,. \tag{20}$$

Equation (20) may be integrated to obtain

$$\ln P = -\frac{\Delta H}{nR}\left[\frac{1}{T}\right] + C, \tag{21}$$

In summary it may be said that application of the Clausius-Clapeyron equation must be to a system which will meet the following requirements:

1. Closed system,
2. Pressure-volume work only,
3. Reversible phase transition,
4. Ideal gas for the gas phase, and
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.

Magnesite and kaolinite were used to compare the use of a calibration curve with the Clausius-Clapeyron equation method of determining ΔH. These materials were selected because studies had been made on each by Stone using his variable pressure apparatus, but no comparisons were made with other methods. Differential curves for these materials are shown in figure 5. A resistance of 400 ohms was used in the differential circuit in both curves shown in figure 5 to permit all of the endothermic peaks to be recorded. The kaolinite curve was not carried to a sufficiently high temperature to observe the exothermic reaction.

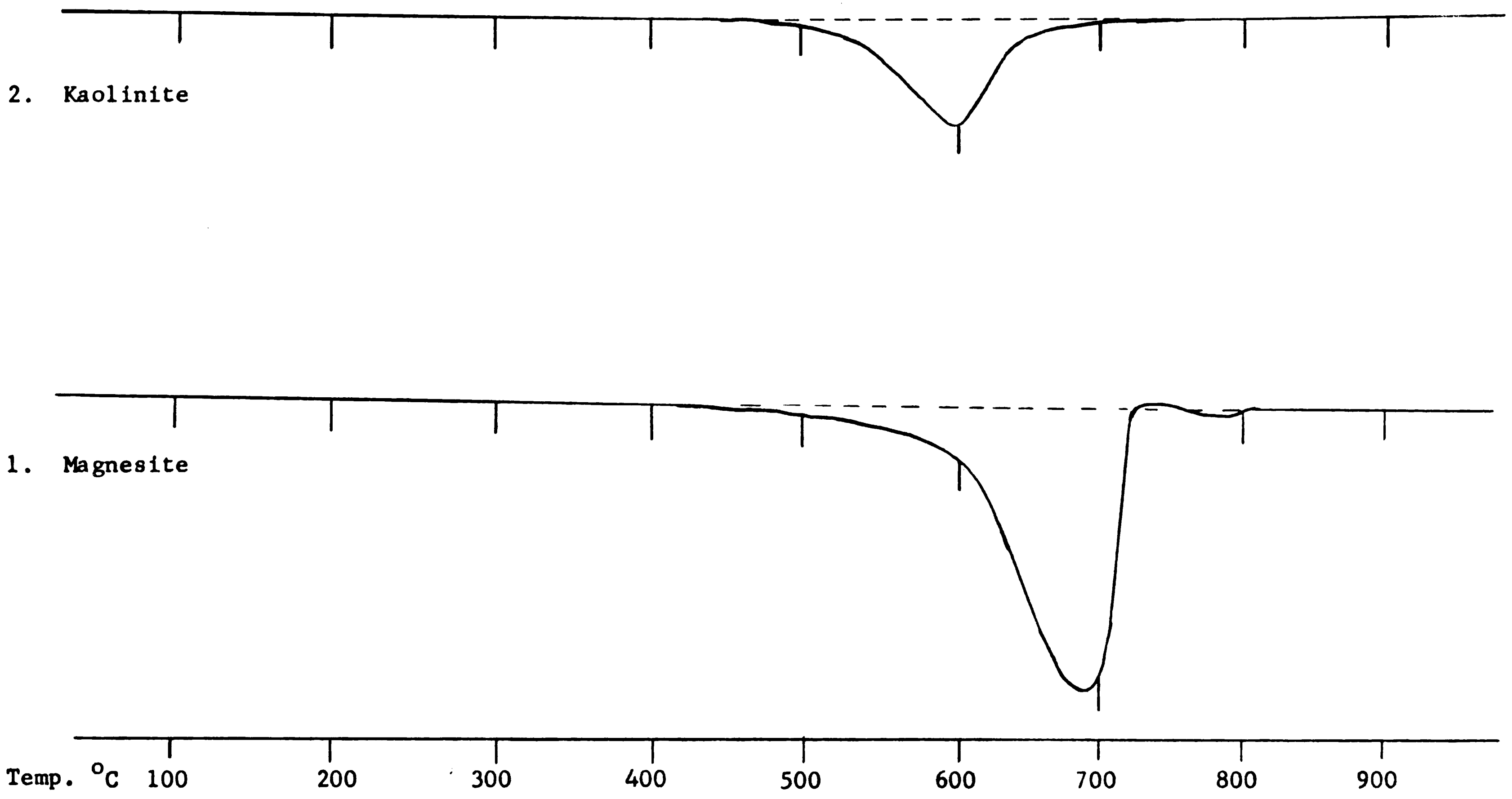


Figure 5. Differential thermal analyses curves of magnesite and kaolinite.

The decomposition of magnesite under variable CO_2 pressures was studied by Stone (31), after which he proposed that the reaction was a straightforward decomposition as given below:

$$MgCO_3 \rightarrow MgO + CO_2. \tag{22}$$

He found that the plot of $\ln P_{CO_2}$ versus $\frac{1}{T}$ gave two straight lines. He attributed deviation in the low pressure region to insensitivity of the recorder. He further stated that there appeared to be a break in the curve at 1810 millimeters of mercury, but his determinations were not carried out at pressures greater than 2200 millimeters of mercury to determine if this deviation is real. Based on his best straight line he calculated a ΔH of decomposition of 10.1 kilocalories per mole of $MgCO_3$. It should be noted that the differential thermal curves shown in Stone's work indicated the presence of an impurity which he attributed to $CaCO_3$. The plot of $\ln P_{CO_2}$ versus $\frac{1}{T}$ is given in figure 6 for magnesite decomposition obtained with the instrument in this work where the pressure was varied from 104 to 3100 millimeters of mercury. Partial pressures below 100 millimeters of mercury were not attempted because the exact determination of the differential pressure is not possible with the instrument used. In this region differential pressure becomes large in comparision with the total pressure and introduces rather large errors in measurement of pressures below 100 millimeters of mercury. As can be seen from figure 6 the data very nearly fits a linear plot even in the low pressure regions. The data deviates from a linear plot in the high pressure regions in a similar manner to data given by Stone. This was not investigated further because examination of the Clausius-Clapeyron equation

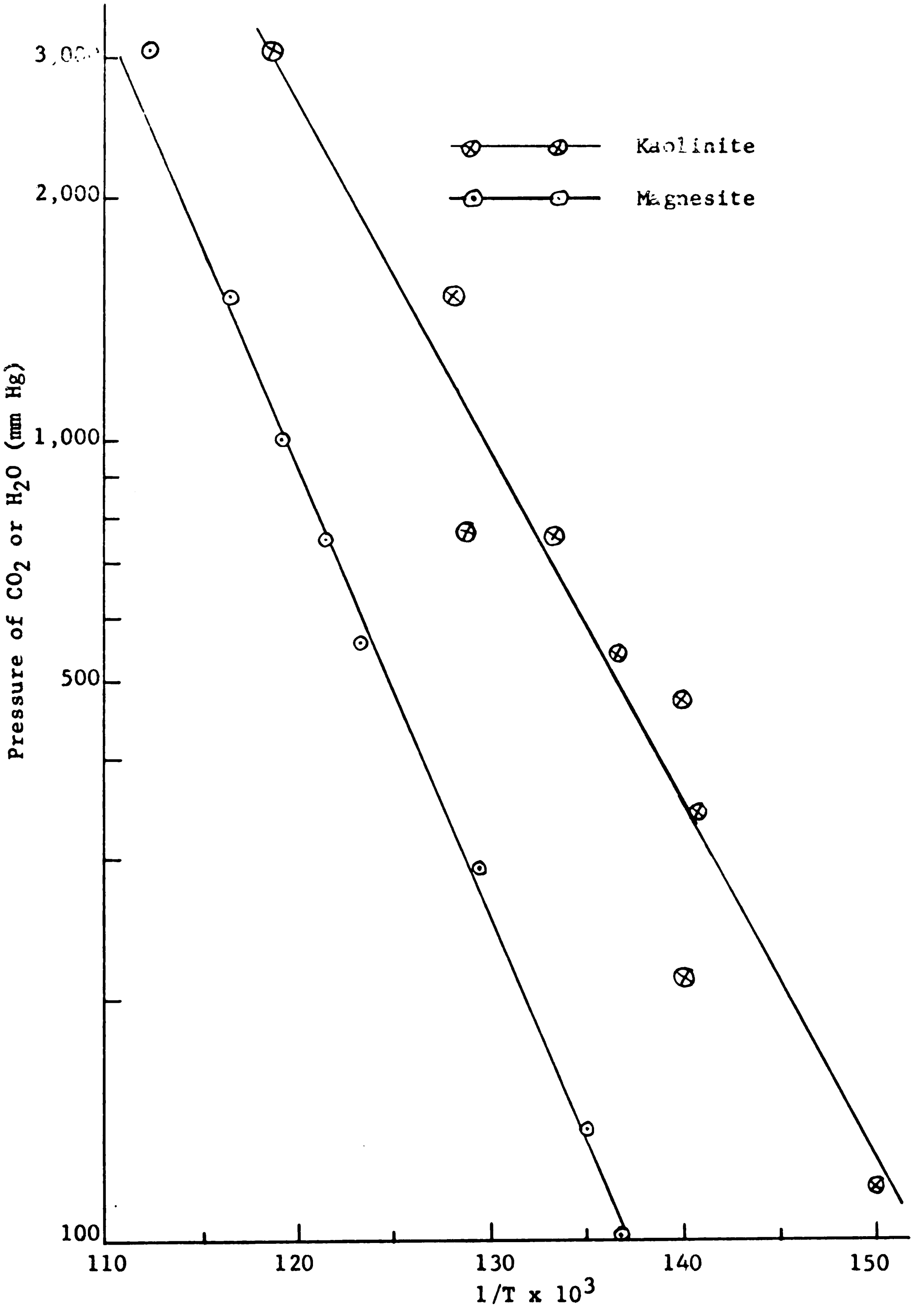


Figure 6. Relationship between decomposition pressure and temperature of magnesite and kaolinite.

predicts that at high pressures where a gas will not behave as an ideal gas and at pressures sufficiently high to cause the volume of the solid or liquid phase to become appreciable in comparison to the gas phase the curve will deviate from a linear plot in the direction determined experimentally. Utilizing the slope from the plot given in figure 6 a value of 27.0 kilocalories per mole of $MgCO_3$ was obtained for its ΔH of decomposition. This value is 16.9 kilocalories per mole greater than that obtained by Stone. The theoretical ΔH may be computed by the following relationship:

$$\Delta H = \sum \Delta H_{products} - \sum \Delta H_{reactants}. \qquad (23)$$

This yields a value of 27.8 kilocalories per mole. The ΔH of decomposition was also determined by use of the calibration curve discussed previously. The value obtained was 28.3 kilocalories per mole assuming that the material was 100 per cent $MgCO_3$. Therefore, the two methods compare quite favorably and also are in good agreement with the value calculated theoretically. The rather large disagreement with the ΔH determined by Stone may be due to impurities in his sample. However, it should be pointed out that the determination utilizing the Clausius-Clapeyron equation is independent of weight of sample used; therefore, impurities should not affect the results unless two reactions occur simultaneously.

The second material used for comparison purposes was kaolinite from Lamar, North Carolina. It was chosen because kaolinite has been studied before and also presents a decomposition which may not be reversible. The reaction for the dehydroxylation has been written by Stone and Rowland (33) as follows:

$$Al_2Si_2O_5(OH)_4 \rightarrow (Al_2O_3 + SiO_2\ Complex) + 2H_2O. \qquad (24)$$

Values for the ΔH of dehydroxylation vary considerably from sample to sample. Van der Marel (35) has reported values from 100 to 176 calories per gram and Stone found values from 140 to 170 calories per gram of clay. The plot of $\ln P_{H_2O}$ versus $\frac{1}{T}$ for kaolinite is shown in figure 6. It can be seen that considerable scatter of points was obtained with kaolinite. The exact reason for this scatter of points is not known; however, some difficulty may be expected in maintaining 100 per cent water vapor for the dynamic gas. The best fit for the points was determined by the method of least squares which yielded the following equation:

$$\ln P_{H_2O} = -10.2 \times 10^3 \left(\frac{1}{T}\right) + 20.13 \qquad (25)$$

Utilizing the slope from this equation a value of 157 calories per gram was obtained as the ΔH of dehydroxylation of kaolinite. A determination of ΔH by use of the calibration curve gave a value of 154 calories per gram of material. Again the two methods compare favorably. It may be noted that the values obtained are in the expected range as reported by other investigators.

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 more than one reaction occurs simultaneously.

CHAPTER III

CLAY CHARACTERIZATION AND PREPARATION

Two clay minerals, bentonite and vermiculite, were used for this study. They were selected because the bentonite will hold large quantities of exchangeable cations with very little fixation, whereas vermiculite will produce considerable fixation of potassium and NH_4 ions.

Wyoming Bentonite

Pure bentonite from Hole 25, Upton, Wyoming, was used as a representative of the montmorillonite clay mineral group. The chemical analysis of this particular sample as recorded in Reference Clay Minerals, American Petroleum Institute Project 49 is given below.

Chemical Analysis

SiO_2	57.49%
Al_2O_3	20.27
Fe_2O_3	2.92
MgO	3.18
CaO	0.23
Na_2O	1.32
K_2O	0.28
H_2O^+	6.85
H_2O^-	7.63
TiO_2	0.12
Total	100.48%

The symbols H_2O^- and H_2O^+ represent water loss below 105 degrees centigrade and above 105 degrees centigrade respectively. The formula suggested for this montmorillonite is $(Al_{1.55}Fe_{.15}Mg_{.33})\ (Al_{.08}Si_{3.92})O_{10}(OH)_2(Na_{.17}\frac{Ca}{2}{.03})$. The montmorillonite family of clay minerals is characterized by high cation exchange capacity arising principally from substitution of magnesium for aluminum in the octhedral layer, high water holding capacity, and swelling properties.

X-ray analysis was conducted by depositing a thin layer of calcium saturated, glycerol solvated clay upon a porous ceramic plate so as to orient the clay particle with respect to the basal plane (001). The oriented sample was then rotated with respect to an X-ray beam produced by copper radiation. The deflections were recorded with a scanning goniometer, utilizing a Geiger-Muller counter tube in conjunction with a scaler-ratio meter with an automatic recorder. In each case a second and third pattern was made of the same sample potassium saturated and heated to 105 and 550 degrees centigrade respectively. The results of the X-ray analysis for the bentonite sample are shown in figure 7. The sample is nearly pure as evidenced by the very intense 17.7 angstrom peak in the pattern of the calcium saturated, glycerol solvated bentonite. Little evidence of impurities is shown except for a small trace of quartz. Differential thermal analysis also indicated a pure sample, but since Chapter IV will deal with differential thermal analysis in detail, no data will be presented at this time.

Both conductimetric and potentiometric titration curves were run as a means of characterizing the clay materials. Since it is a

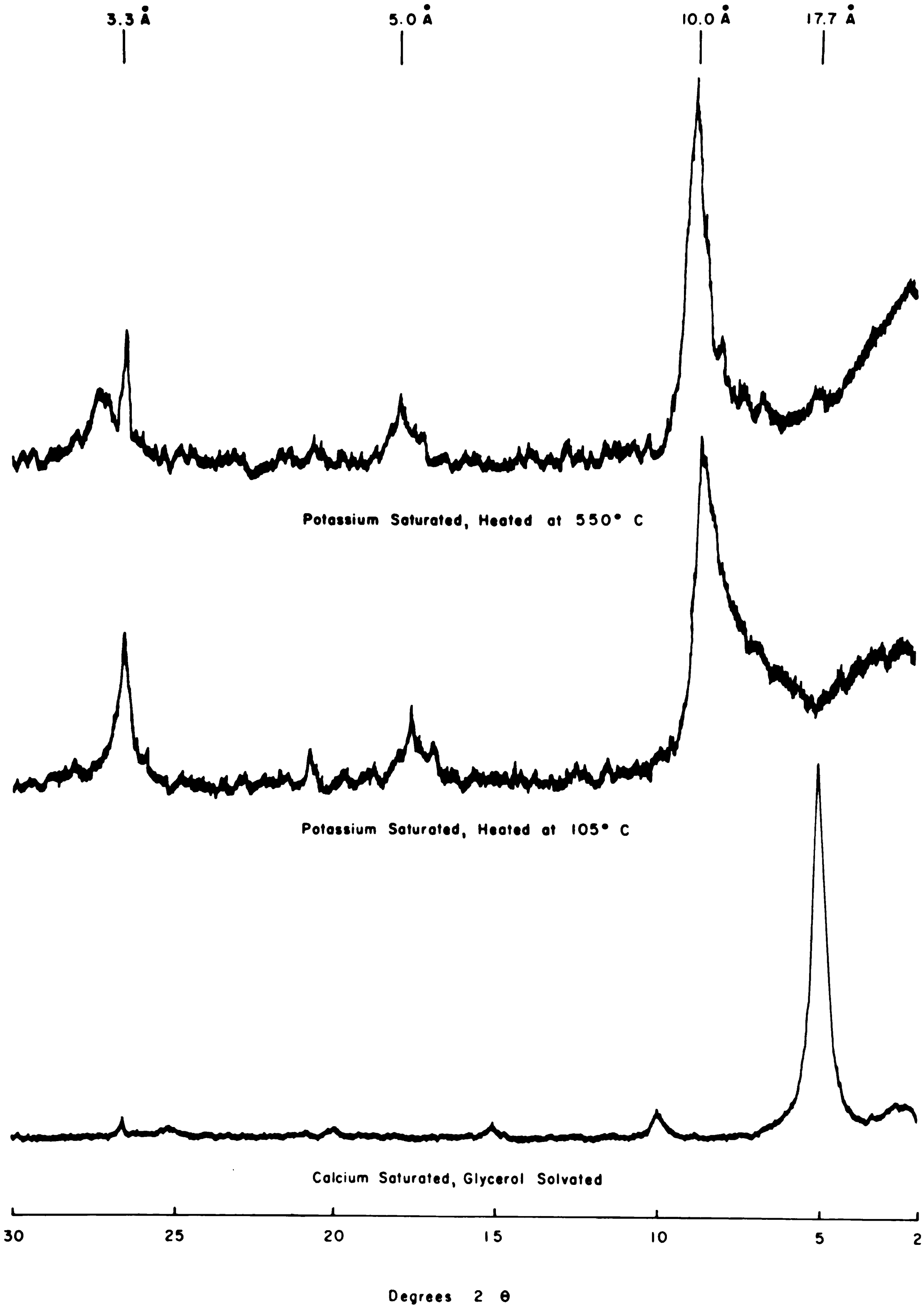
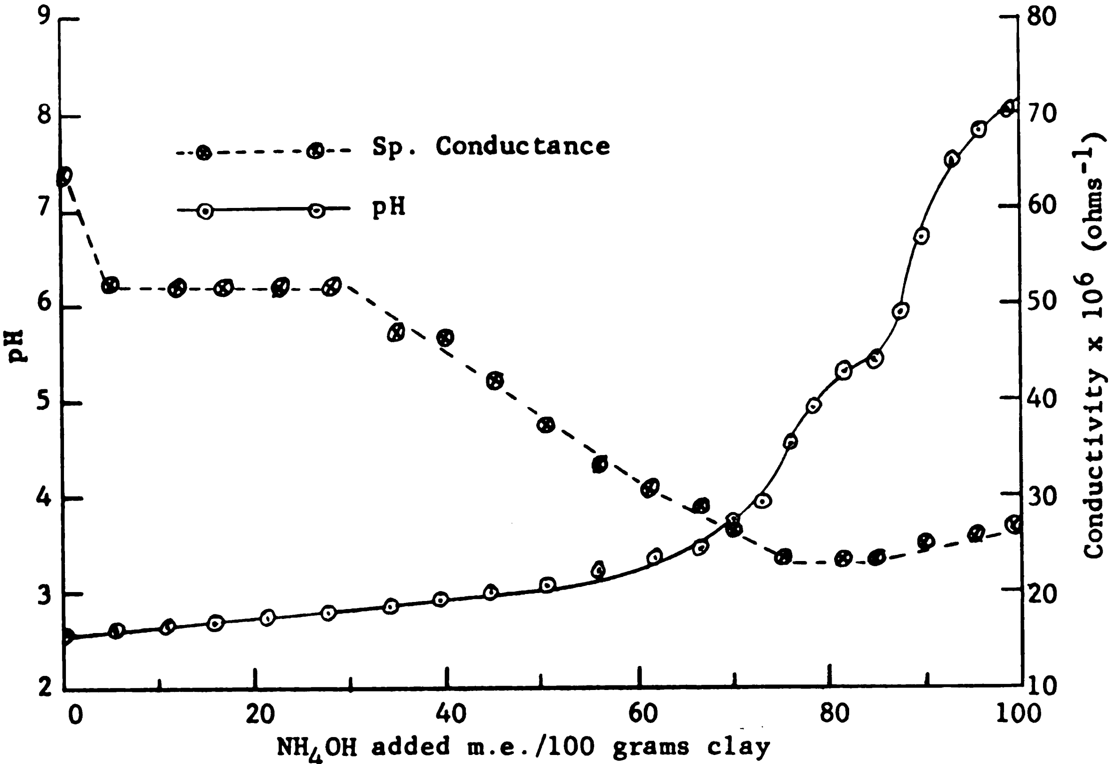


Figure 7. X-ray diffraction patterns for bentonite from Upton, Wyoming.

well established fact that most clay minerals may contain large quantities of exchangeable aluminum, the bentonite clay was prepared by three different methods to yield different degrees of aluminum saturation. The minimum amount of aluminum saturation was obtained by passing a bentonite clay suspension through hydroxyl saturated Amberlite IR-45 anion exchange resin and then through hydrogen saturated Amberlite IR-120 cation exchange resin. The titration of the clay was started approximately fifteen minutes after the first bentonite had passed through the IR-120 resin and was finished approximately one hour later. The results of titration curves made using both NaOH and NH_4OH are given in figure 8. Both the NaOH and the NH_4OH curves indicate a cation exchange capacity of approximately 90 milliequivalents per 100 grams clay of which approximately 15 milliequivalents per 100 grams clay is exchangeable aluminum. To obtain a bentonite clay which was moderate in the amount of exchangeable aluminum the clay was electrodialyzed to a pH of 3.3. Titration curves for this material are shown in figure 9. The cation exchange capacity of this sample appears to be 74 milliequivalents per 100 grams of clay of which 31 milliequivalents are exchangeable aluminum. Two factors may account for the apparent lowering of the cation exchange capacity. First, electrodialysis may not successfully remove all exchangeable bases, and secondly, the treatment undoubtedly results in some breakdown of the mineral lattice. An aluminum saturated clay was prepared by passing the clay material through an aluminum saturated IR-120 exchange resin. The resin was aluminum saturated by leaching with $AlCl_3$ solution and then washing with distilled water until the leachate was free from chlorides as



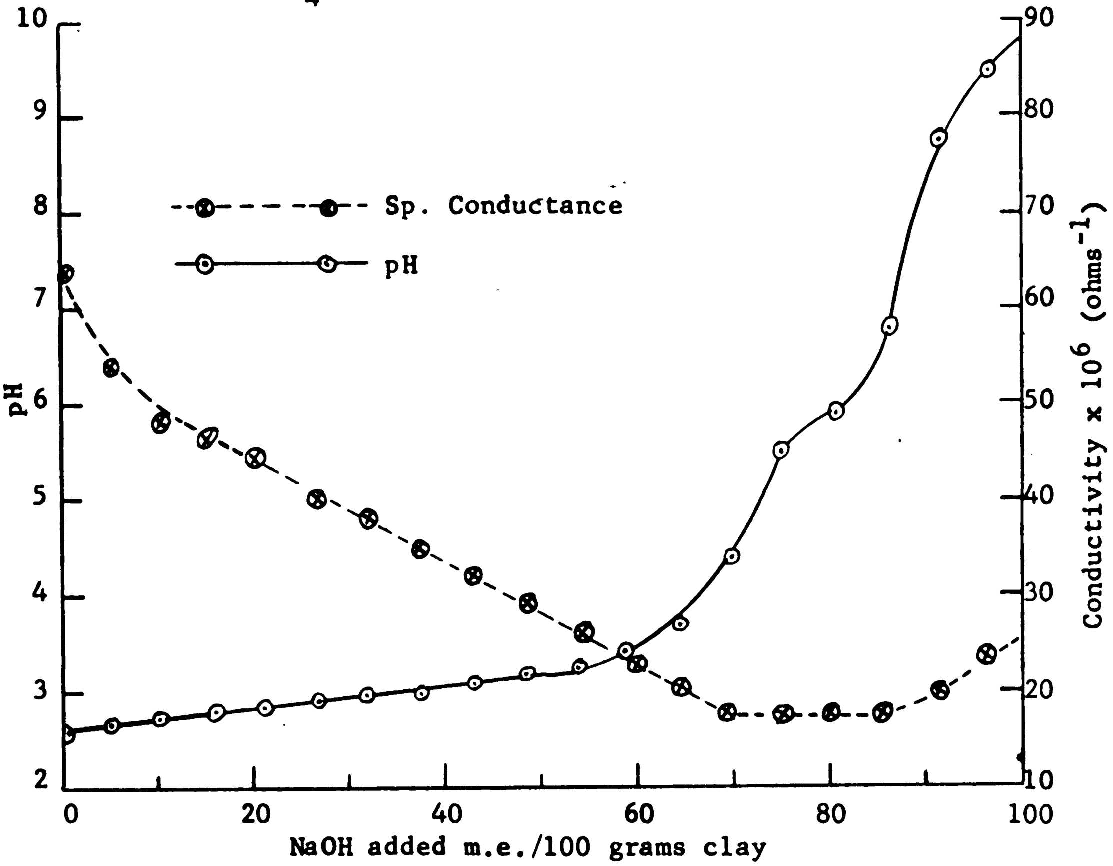
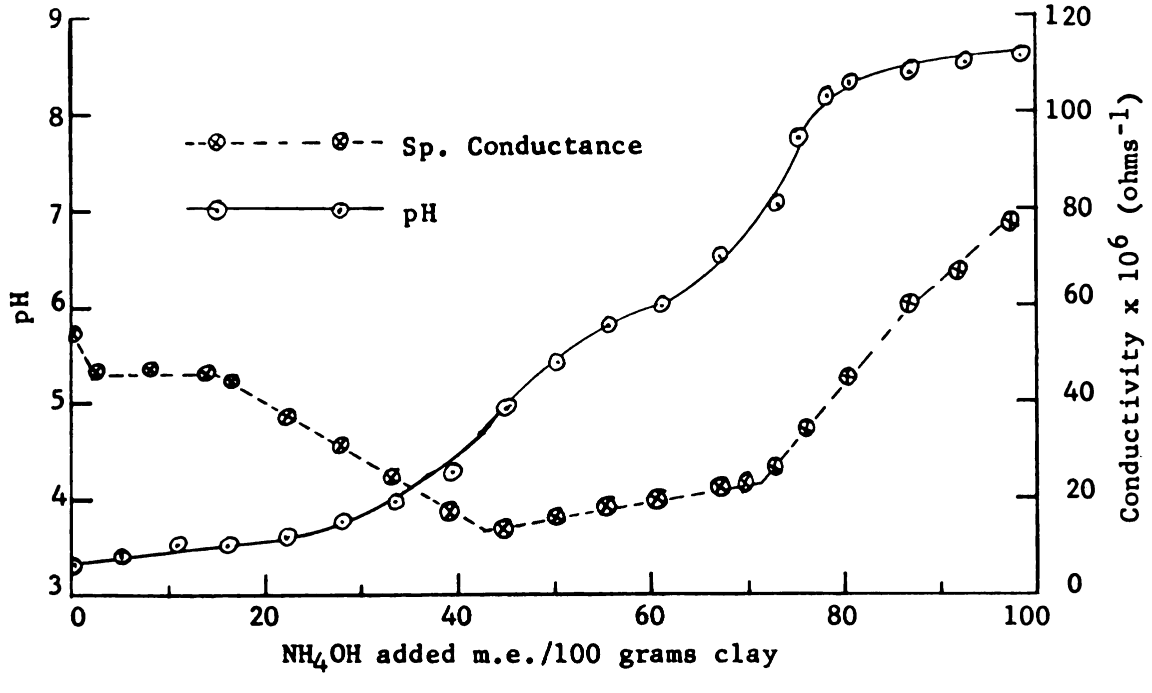


Figure 8. Titration curves of bentonite hydrogen saturated by use of a H-Resin.



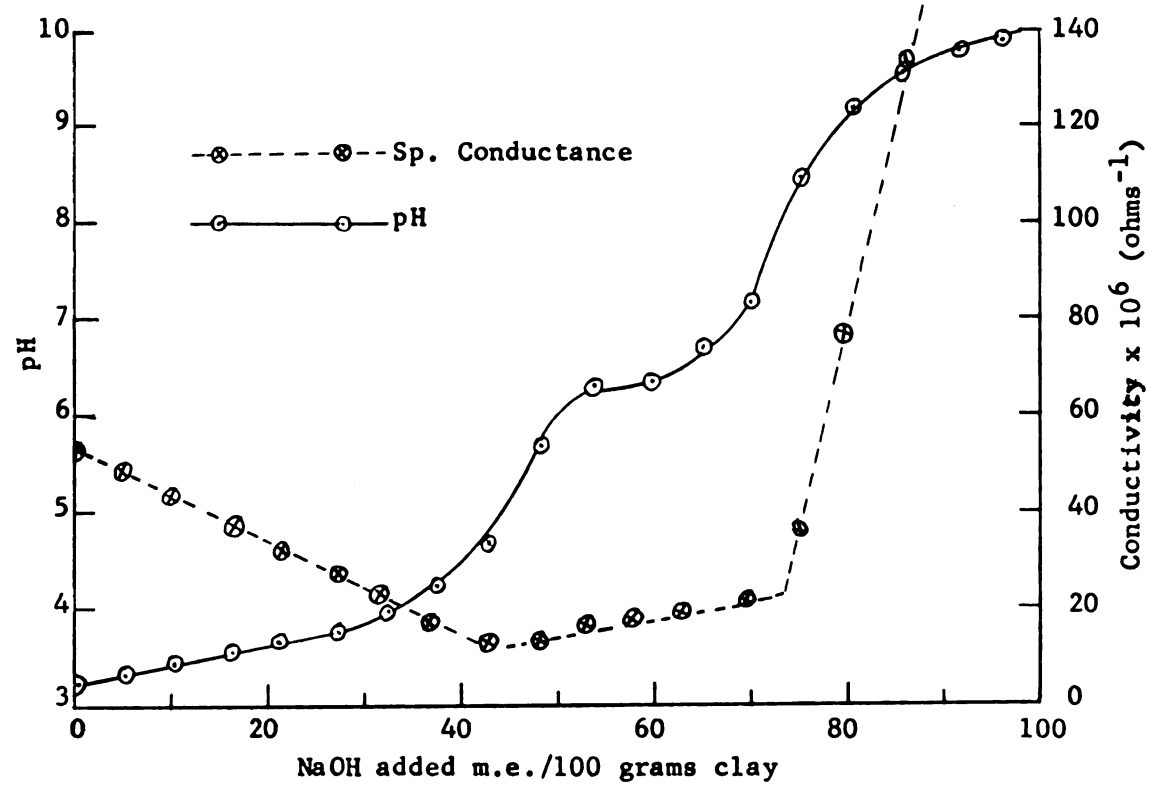


Figure 9. Titration curves of bentonite hydrogen saturated by electrodialysis.

indicated by $AgNO_3$. One difficulty was encountered in that the clay material flocculated upon contact with the exchange resin and was then very difficult to extract from the resin column. The saturation was accomplished by using short columns, frequent recharging with $AlCl_3$, and slight suction from a water aspirator to draw the clay suspension through the resin column. The titration curves of this material are shown in figure 10. It is evident that the clay material is almost one hundred per cent aluminum saturated. The titration curves show poorer defined breaks in this case, but at pH 7.0 the material should still contain nearly 75 milliequivalents of NH_3 per 100 grams of clay.

To prepare NH_3 saturated clays for differential thermal analysis the clay materials were hydrogen saturated and/or aluminum saturated as described above and then immediately titrated to pH 7.0 with 1N NH_4OH, stirred overnight with a magnetic stirrer, and then readjusted to pH 7.0. This process was repeated until the equilibrium pH was 7.0. At this time the material was dried under an infrared light, ground in a mortar and pestle, thoroughly mixed, and stored in a desiccator until differential thermal analyses were run.

Methylamine saturated samples were prepared by adding 10 milliliters of 40 per cent methylamine in water to the freshly prepared hydrogen saturated clay and shaking for 48 hours. The material was then dried under an infrared light, ground with a mortar and pestle, and dried at 60 degrees centigrade under vacuum. During the drying the excess methylamine was volatilized leaving the clay methylamine saturated.

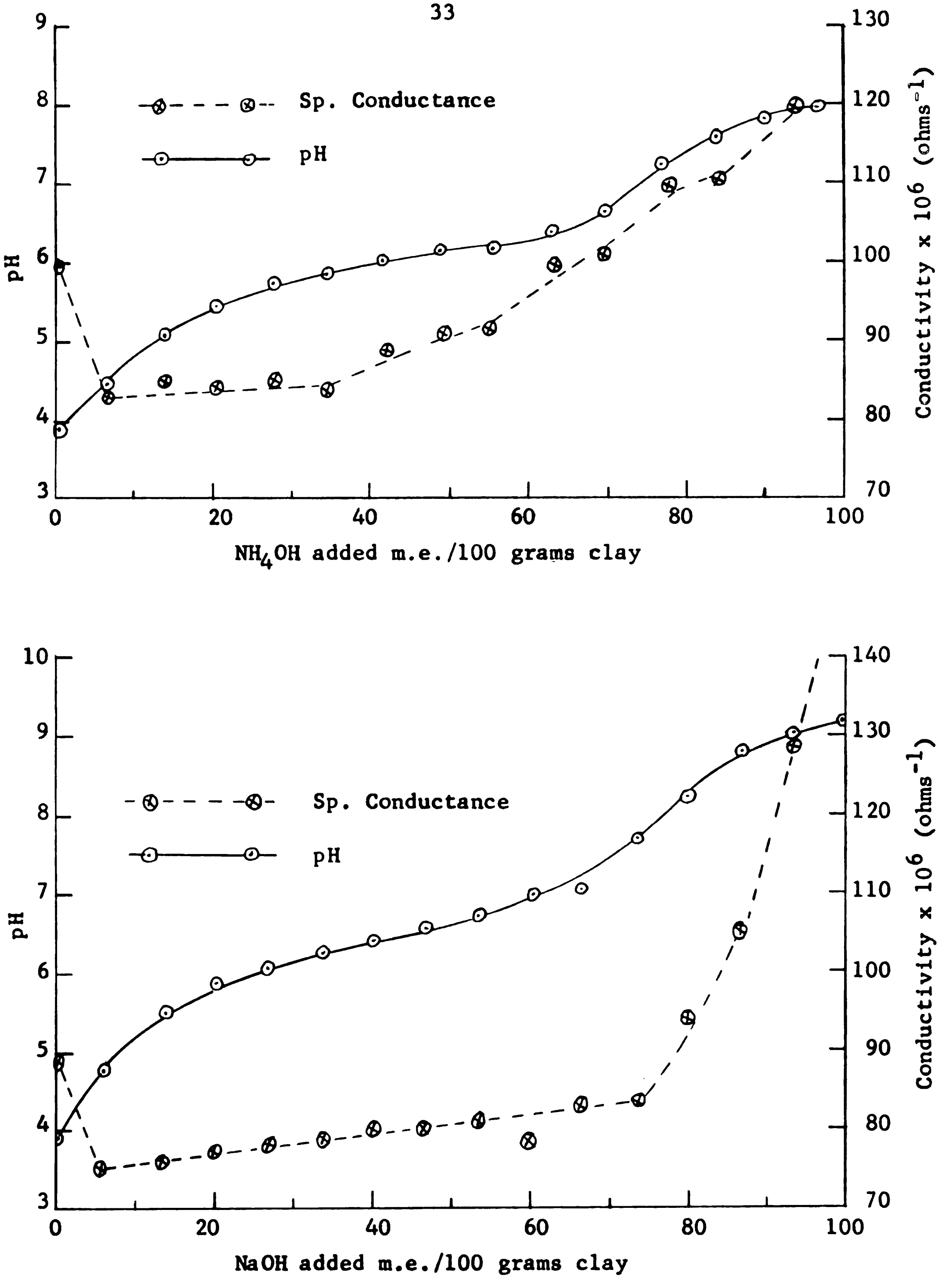


Figure 10. Titration curves of aluminum saturated bentonite.

The bentonite clay was saturated with ethylamine by two different procedures. The procedure utilized in the first replication was to hydrogen saturate the bentonite clay with a hydrogen resin column and then to treat the hydrogen saturated clay with ethylamine gas. The ethylamine gas was introduced into a glass tube containing approximately 300 milliliters of the clay suspension through a one-holed rubber stopper fitted with a glass tube and stopcock. Approximately 20 milliliters of liquid anhydrous ethylamine were vaporized and passed into the clay material. The clay suspension was then transferred to a flask, stoppered, and stirred for 48 hours with a magnetic stirrer. After stirring, the material was dried under an infrared lamp, ground with a mortar and pestle, and further dried at 60 degrees centigrade under vacuum. The second replication of ethylamine saturated bentonite was prepared by adding 20 milliliters of ethylamine previously cooled to zero degrees centigrade to a suspension containing 10 grams bentonite. The mixture was stirred for 48 hours with a magnetic stirrer and dried similarly to the first replication.

Although it would be expected that organic materials possessing reactive carboxyl or hydroxyl groups would not be held as exchangeable ions to any large extent by clay minerals, it was felt that quantities detectable by differential thermal analysis might be adsorbed. Thus, two organic acids, formic and acetic acid, and two alcohols, methanol and ethanol, were selected for study. To prepare the clay-acid materials, a large excess of formic or acetic acid was added to a suspension of bentonite clay and shaken on a shaker for 48 hours. The excess acid was then removed by dialysis. The clay-alcohol samples were prepared by placing dry bentonite in absolute methanol or ethanol and shaking on a shaker for 48 hours. The excess alcohol was then removed by evaporation. Both the acid- and alcohol-clay samples were dried under an infrared lamp.

Vermiculite

Zonolite, a vermiculite which may be obtained commercially, was used as a representative from this group of clay minerals. The material was ball-milled for 24 hours to reduce the particle size without destroying the crystal structure. Samples of zonolite typically contain considerable interlayer potassium which must be removed to obtain a uniform, homogeneous vermiculite sample. The sample of zonolite utilized in this study was leached with approximately 0.5 N NaCl at a slow leaching rate for a period of two months to remove this interlayer potassium. The total potassium remaining at this time was 2.99 per cent. After this leaching process, the sodium saturated vermiculite was dispersed in a water system and a separation of the less than two micron material made utilizing Stoke's law.

Perhaps the best single method of identifying and characterizing vermiculite is X-ray analysis. The results of this analysis carried out in a similar manner as for bentonite are given in figure 11. The 14.8 angstrom peak, characteristic of a calcium saturated vermiculite, is very intense. However, some indication of interstratification of the mineral is shown by the broadening of the peak as it returns to the base line. The potassium saturated sample heated to 105 degrees centigrade collapsed to 10 angstroms

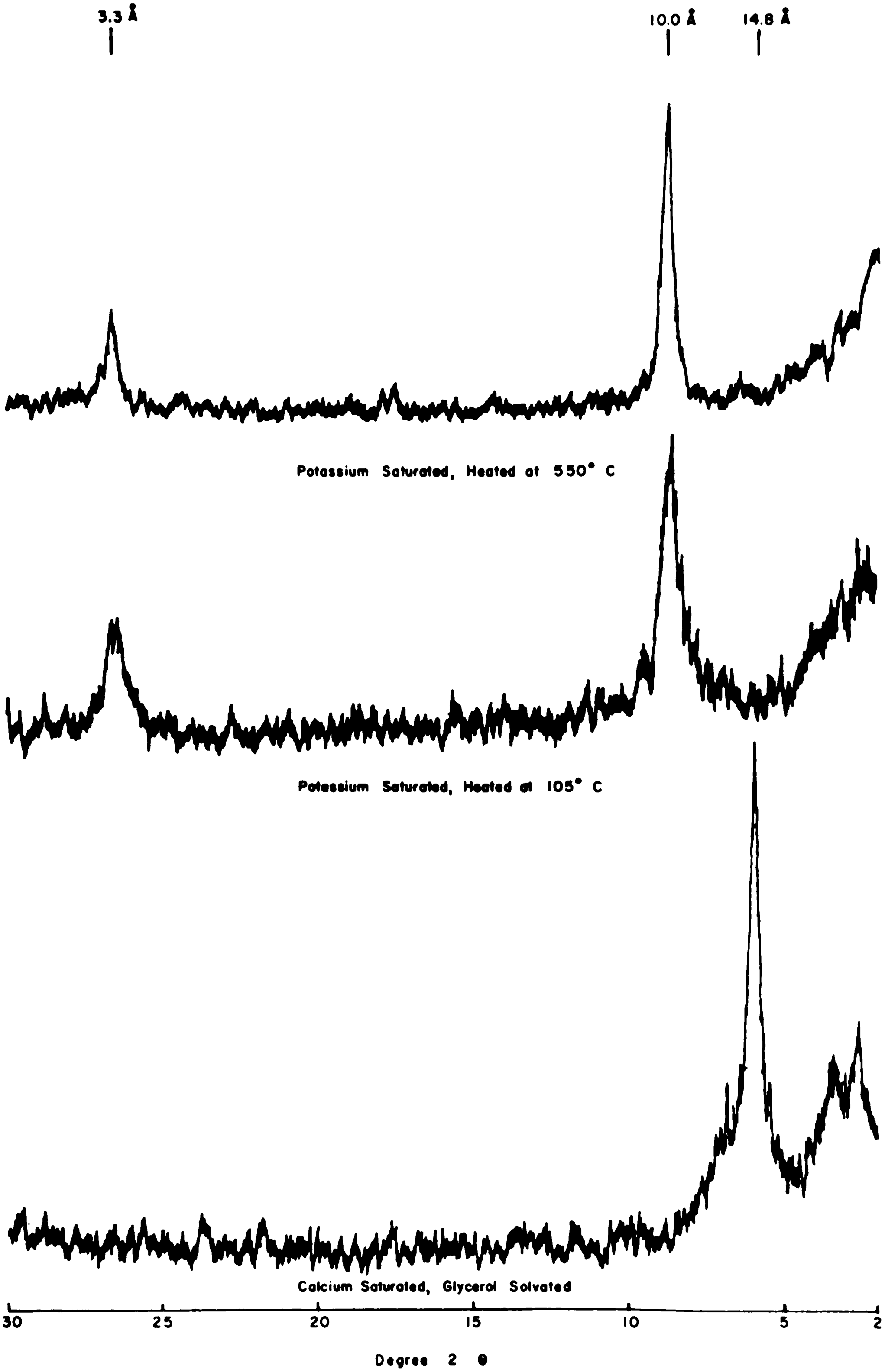


Figure 11. X-ray diffraction patterns for less than two micron vermiculite.

as would be expected. Although heating to 550 degrees centigrade had little effect on the basal spacing, it did sharpen the peak considerably.

Titration curves using NaOH are shown in figure 12. However, for vermiculite this proved to be a poor method of characterizing the clay mineral. No sharp endpoints are indicated in the curve.

Because the titration curves did not yield a good measure of the cation exchange capacity, it was determined by the procedure described by Ellis and Mortland (6). The cation exchange capacity as determined by this method is 114 milliequivalents per 100 grams clay. It should be noted that cation exchange capacities determined by this means may be slightly high due to removing sodium ions from the mineral lattice.

Samples of vermiculite were prepared saturated with NH_3, methylamine, and ethylamine. The method of sample preparation was the same as for bentonite except for ethylamine. For ethylamine the procedure followed for the second replication of bentonite was utilized. It was necessary to pass the vermiculite suspension through the hydrogen resin column many times to obtain a hydrogen saturated clay. Therefore, the vermiculite undoubtedly contained considerable exchangeable aluminum.

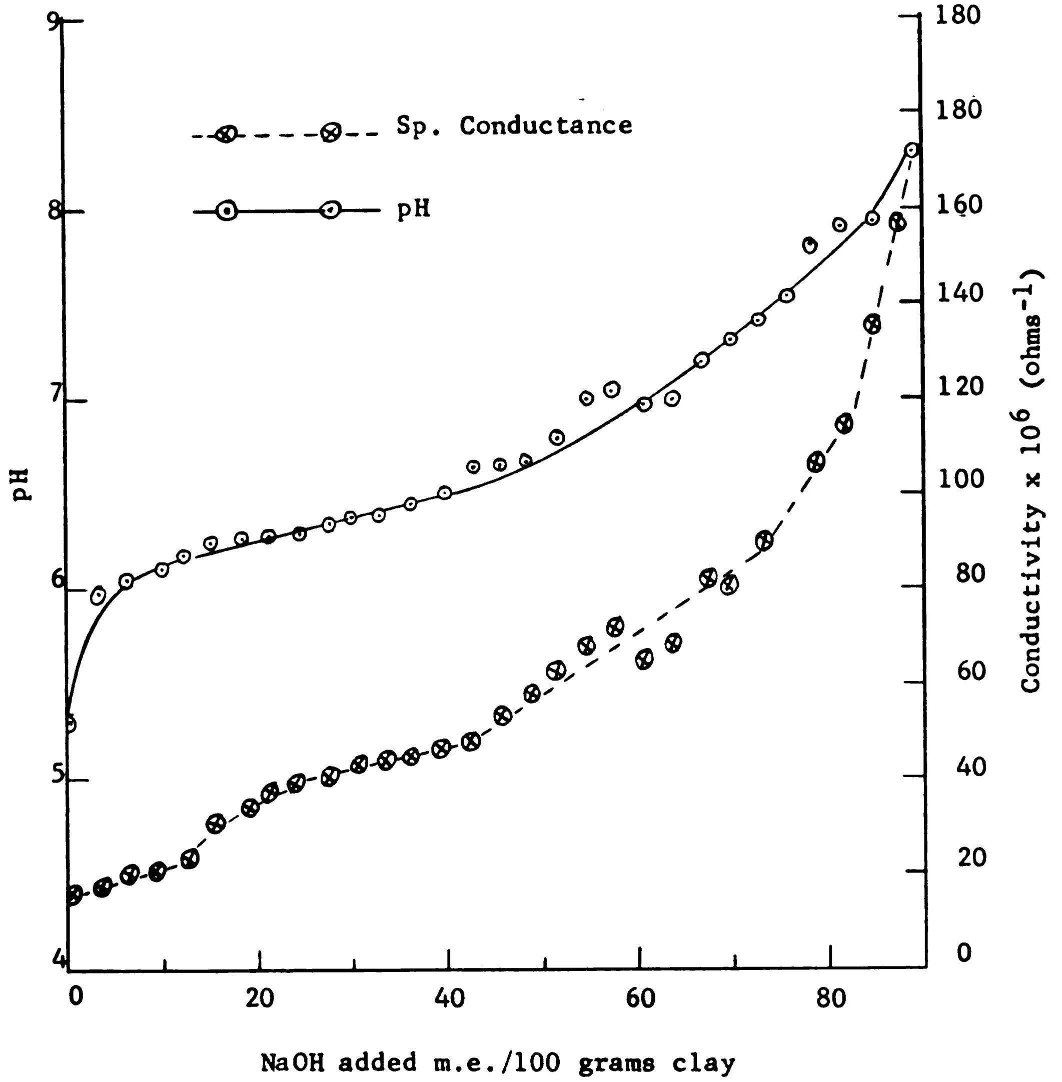


Figure 12. Titration curves of hydrogen saturated vermiculite.

CHAPTER IV

DIFFERENTIAL THERMAL STUDIES OF WYOMING BENTONITE

Importance of Ammonia Reactions in Soils

Anhydrous NH_3 has been used as a nitrogen fertilizer during the past several years. Retention of NH_3 by soils has been largely attributed to the formation of NH_4 ions and subsequent attraction of the NH_4 ions by the cation exchange complex. McDowell and Smith (16) reported that soil texture had a pronounced effect on NH_3 movement and retention in soils. They found that the greatest movement occurred in sand and silt loam soils and the least movement in clay soils. Sohn and Peech (27) attributed the capacity of a soil to sorb NH_3 to neutralization of exchangeable hydronium and aluminum ions as well as to the formation of organic nitrogen compounds upon autoxidation of soil organic matter and simultaneous NH_3 fixation. An extensive review of the importance of NH_3 and its reactions in the soil has been given by Mortland (19).

Differential Thermal Curves of Ammonia Saturated Montmorillonite

In the past various attempts have been made to relate the temperature at which NH_3 is lost from clay minerals with its adsorption site. Cornet (5) suggested that NH_4 ions on broken bond surfaces were decomposed at temperatures below 125 degrees centigrade while rapid loss of NH_4 ions from 275 to 400 degrees centigrade was from NH_4 ions on planar surfaces. Mortland (19) suggested that ammonia chemically sorbed by clay minerals probably does not exist at discrete energy levels, but that a wide range exists in the energy of chemical sorption of ammonia by clays. Scott, et al. (25) found differential thermal analysis curves of NH_4-bentonite exhibited exothermic peaks near 550 degrees centigrade. They drew the following conclusions:

> The exothermic peak in the bentonite differential thermal curves occurred in all cases where fixed NH_4 was present. If the NH_4 ions were blocked from the fixing sites by prior fixation of K, the curve exhibited no exothermic effects from NH_4 ions on the bentonite. Apparently any exothermic effect due to the loss of NH_3 from the exchangeable NH_4 ions is counteracted by a concurrent loss of water. On the other hand, the fixed NH_4 ions are decomposed and NH_3 lost without a concurrent loss of water, since an exothermic peak occurs. This indicates that the exchangeable NH_4 ions in bentonite are closely associated with water molecules while the fixed NH_4 ions are not.[1]

This suggested a system in which the heat of desorption of ammonia could be measured by differential thermal analysis to yield valuable information in differentiating between exchangeable and fixed NH_3. Preliminary studies yielded a differential thermal analysis curve of NH_3 saturated bentonite similar to that shown as curve 1, figure 13. The appearance of the exothermic peak near 550 degrees centigrade is very similar to that noted by Scott. However, in trying to predict the reaction which is occurring, great difficulty is encountered. The breakdown of NH_4 ions to yield NH_3 and subsequent

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[1] A. D. Scott, J. J. Hanway, and G. Stanford, "Thermal Studies of Ammonium Fixation and Release in Certain Clay Minerals," American Mineralogist, 47:718, 1956.

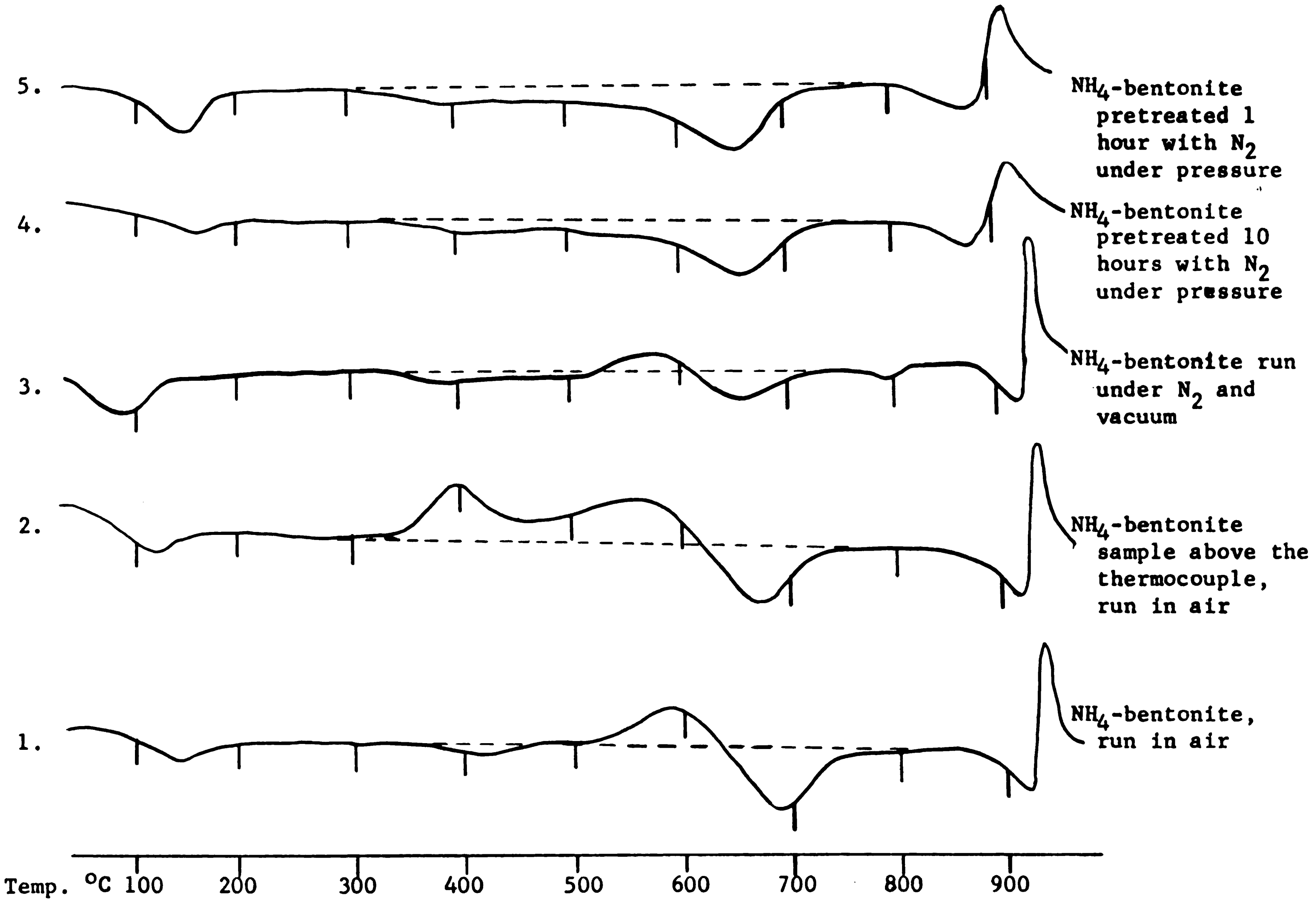

Figure 13. The effect of various treatments on the oxidation of NH_3 during differential thermal analysis; one-sixteenth actual size.

evolution of NH_3 should, in fact, yield an endothermic reaction. An estimate of the heat of reaction obtained from heats of formation data is 20.1 kilocalories per mole of NH_3 evolved. No plausible explanation could be found for a simple breaking of the clay-NH_3 bond or simple dissociation of NH_4 ions which would yield an exothermic reaction. Barshad (3), however, found similar difficulties with NH_4NO_3 used in temperature calibration of the differential thermal analysis apparatus. He noted that large exotherms appeared when NH_4NO_3 was used and suggested that these were due to the oxidation of NH_3 catalyzed by the platinum thermocouples. He suggested that this oxidation could be prevented by layering the NH_4NO_3 above the thermocouple instead of below or surrounding the thermocouple.

To verify Barshad's suggestion a simple semiquantitative experiment was designed to ascertain if NH_3 was oxidized by heat and if this reaction is enhanced by a platinum catalyst. Samples of NH_3 saturated bentonite were placed in a test tube equipped with a two-holed stopper arranged so that glass tubing from one hole led into a boric acid trap and glass tubing from the other hole allowed one to blow into the test tube and flush the component gases through the boric acid trap. The test tube containing the NH_4-bentonite was heated with a Bunsen burner to a maximum heat and then the gases flushed into the boric acid. The boric acid was subsequently titrated with standard HCl to determine the quantity of NH_3 evolved. This process was repeated with Al_2O_3 mixed with the NH_4-clay, and with Al_2O_3 and a piece of platinum wire present in the test tube. Results of this experiment are given in Table II.

Although the results given in Table II are semiquantitative in nature, they effectively show that NH_3 is eliminated and presumedly oxidized by heat when a platinum catalyst is present. It would thus appear that the exothermic peak which Scott has attributed to release of fixed NH_4 ions is nothing more than the catalytic oxidation of NH_3 in a reaction which follows the dissociation of the NH_3 from the clay mineral and is in no way related to its position on the clay mineral.

TABLE II

THE OXIDATION OF NH_3 RELEASED FROM BENTONITE CLAY

Treatment	NH_3 Recovered m.e./100 gms Clay	NH_3 Recovered (%)
none	61	64.0
Al_2O_3 Added	65	69.0
Al_2O_3 + Pt Wire	10	10.8

The problem then reverted to one of eliminating oxidation of NH_3 during the heating of the sample in differential thermal analysis. Theoretical considerations would completely rule out application of Barshad's suggestion to layer the sample containing NH_3 above the thermocouple since this could produce a nonsymetrical orientation of the sample with respect to the thermocouple and produce a vertical heat flow gradient. Nevertheless, this method was attemped during the course of investigation of methods to eliminate the oxidation of the NH_3. The resulting curve is shown as curve 2 in figure 13. It should be noted that the sensitivity of the instrument was increased greatly in order to record the smaller heat changes registered by the thermocouple. The results still showed the exothermic reaction. Since the instrument used in this study is equipped to run a sample under a controlled atmosphere at elevated pressures, atmospheric pressure, or under vacuum, it appeared that the oxidation might be prevented by use of an inert gas such as nitrogen during the run. The first procedure investigated involved evacuation of the system and subsequent introduction of nitrogen gas through the sample and into the chamber. This was repeated three times and the differential thermal analysis made with the sample under vacuum. The resulting curve is shown as curve 3 in figure 13. Again the exothermic peak persists. The failure of this method may be attributed to slight leakage in the manifold of the differential thermal apparatus which introduced oxygen into the system and sample while the evacuation process was being utilized. The final method tested, and the one which proved to be effective, was that of evacuating the system and then introducing nitrogen gas under a slight pressure. The nitrogen gas was purified by passing it through a pyrogallic acid trap and a H_2SO_4 trap. This procedure was repeated three times and then the sample was allowed to pretreat with nitrogen passing through it at a pressure of slightly greater than one atmosphere. The flowing gas was stopped and the pressure reduced to atmospheric pressure prior to making a differential thermal analysis. Thus, the determination was made under static conditions with no vertical heat flow gradients produced by a flowing gas. Various pretreatment times were tested. Two curves of the same sample, but one pretreated for ten hours and the other pretreated for one hour, are shown as curves 4 and 5 respectively in figure 13. No difference could be noted between the two curves; therefore, a one hour pretreatment was utilized for preventing oxidation in the remaining studies conducted in this work.

Examination of the differential thermal analysis curve, which resulted from an NH_3 saturated bentonite clay once oxidation had been eliminated, presented rather large difficulties to quantitative heat of reaction measurements. It was apparent that the loss of NH_3 was not homogeneous in nature. Indeed, once the differential thermal curve deviated from the base line near 250 degrees centigrade due to the loss of NH_3, it did not return to the base line until after the completion of dehydroxylation of the mineral near 750 degrees centigrade. Thus, the lack of homogeneity ruled out the application of the Clausius-Clapeyron equation to this system and the intermixing of two reactions coupled with the long departure of the curve from the base line seriously limited the applicability and accuracy of the method of area determinations. It was noted, however, that the curve did return to the base line once dehydroxylation was complete which would theoretically justify the use of area determinations as a quantitative measure of the heat of reaction.

Due to the complexity of the reactions involved in loss of NH_3 from bentonite, it was necessary to determine the change in area of the differential thermal analysis curve after a portion of the NH_3 had been removed by heating to obtain an estimate of the heat of reaction when NH_3 is evolved. This was accomplished by placing samples of NH_3 saturated bentonite in platinum crucibles, weighing them, and then heating the samples for a period of time to remove a portion of the NH_3. The samples were then reweighed to determine the total loss in weight upon heating. Differential thermal analysis was conducted on subsamples before and after heating. Examples of these curves are shown in figure 14. Subsamples were taken and NH_3 determined by a modified semi-micro Kjeldahl process. The determination was accomplished by digesting a 0.1 gram sample of the clay material with concentrated sulfuric acid and a salt mixture of K_2SO_4 and $CuSO_4$. The mixture was digested over a Bunsen burner until the solution became a bright green and then digested for an additional hour. The flask was allowed to cool, a small amount of distilled water added, and then the flask cooled in a water bath. After the flask and contents were cool, a sufficient quantity of solid NaOH was added to make the final digestion mixture basic as evidenced by a dark brown color, and then the NH_3 was voltalized by steam distillation. The NH_3 was trapped in 40 milliliters of two per cent boric acid and titrated with 0.0196 N HCl to a gray end point with a methyl red, methylene blue indicator.

The heats of reaction calculated for the loss of NH_3 from bentonite for the temperature range 200 to 450 degrees centigrade are given in Table III. Two points in Table III are of considerable interest. First, all values obtained for the heats of reaction are considerably higher than the theoretical 20.1 kilocalories per mole for the formation of NH_3 from NH_4^- ions. Second, the heat of reaction is larger for the bentonite which had been hydrogen saturated by electrodialysis. At this point it must be recalled that the differential thermal analysis apparatus records only the net heat change occurring during a reaction and thus, for proper

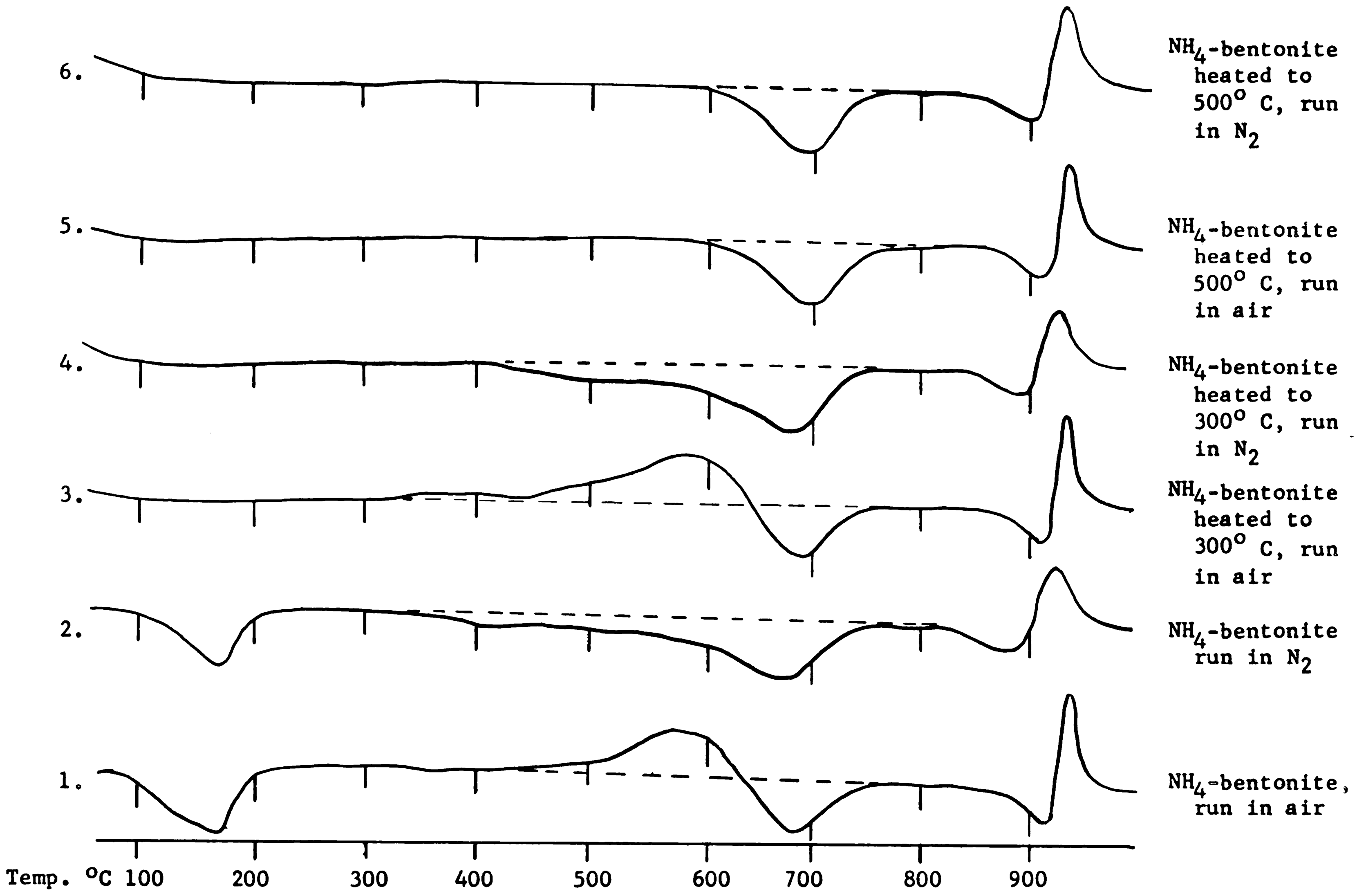

Figure 14. Differential thermal analyses curves of NH_3 saturated bentonite; one-sixteenth actual size.

interpretation of heat of reaction data we must know the reactions which are occurring.

TABLE III

THE HEAT OF REACTION OF NH_3 RELEASED FROM NH_4-BENTONITE*

Temperature Range °C	Hydrogen Saturated by Resin, NH_3 Saturated ΔH (K Cal/mole)**	Hydrogen Saturated by Electrodialysis, NH_3 Saturated ΔH (K Cal/mole)**
200-300	35.3	41.8
300-400	37.0	41.0
250-350	35.2	52.7
350-450	33.6	59.1

*Values for temperature ranges 200-300 and 300-400 are from one sample while values for the temperature ranges 250-350 and 350-450 are from another sample preparation.

**Expressed as kilocalories per mole of NH_3 evolved.

Further information concerning the reaction or reactions occurring in this system may be obtained from the weight loss data given in Table IV. It is apparent that the entire weight loss may not be attributed to loss of NH_3. The most probable constituent to be lost other than NH_3 is water. It is also evident that this loss, presumably water, is continuous. The dry weight of the clay free of water and NH_3 used in Table IV was obtained by assuming that NH_3 lost above 400 degrees centigrade had the same amount of water associated with it as that NH_3 lost between 200 and 400 degrees centigrade. For purposes of illustration the data for NH_3 and water lost from bentonite are summarized in figure 15. It should be emphasized that each point above 250 degrees centigrade

TABLE IV

THE TOTAL WEIGHT, WATER, AND NH_3 LOST FROM BENTONITE WHICH HAD BEEN HYDROGEN SATURATED BY A RESIN COLUMN AND THEN NEUTRALIZED WITH NH_4OH

Initial Temp. °C	Final Temp. °C	Time (hrs.)	Total Wt. Lost (gms/100gms)*	Water Content (gms/100gms)*	Water Lost (gms/100gms)*	Dehydroxylation*	NH_3 Content (gms/100gms)*	NH_3 Lost (gms/100gms)*
--	--	--	0.00	10.05	0.00	0.00	1.42	0.00
60	& Vacuum	1.5	2.65	7.42	2.63	0.00	1.40	0.02
60	& Vacuum	1.5	3.70	3.63	3.79	0.00	1.49	-0.09
60	& Vacuum	10	1.43	2.19	1.44	0.00	1.50	-0.01
60	200	10	0.54	1.73	0.46	0.00	1.42	0.08
200	300	10	0.81	1.28	0.45	0.00	1.06	0.36
300	400	10	0.95	0.77	0.51	0.00	0.62	0.44
400	500	10	1.49	0.13	0.64	0.33	0.10	0.52
500	600	10	2.29	0.00	0.13	2.06	0.00	0.10
60	& Vacuum	--	0.00	2.03	0.00	0.00	1.57	0.00
60	250	10	0.55	1.63	0.40	0.00	1.42	0.15
250	350	10	0.87	1.21	0.42	0.00	0.97	0.45
350	450	10	0.99	0.74	0.47	0.14	0.59	0.38
450	550	10	1.93	0.22	0.52	0.99	0.17	0.42

*Expressed as grams per 100 grams of water free, NH_3 free bentonite.

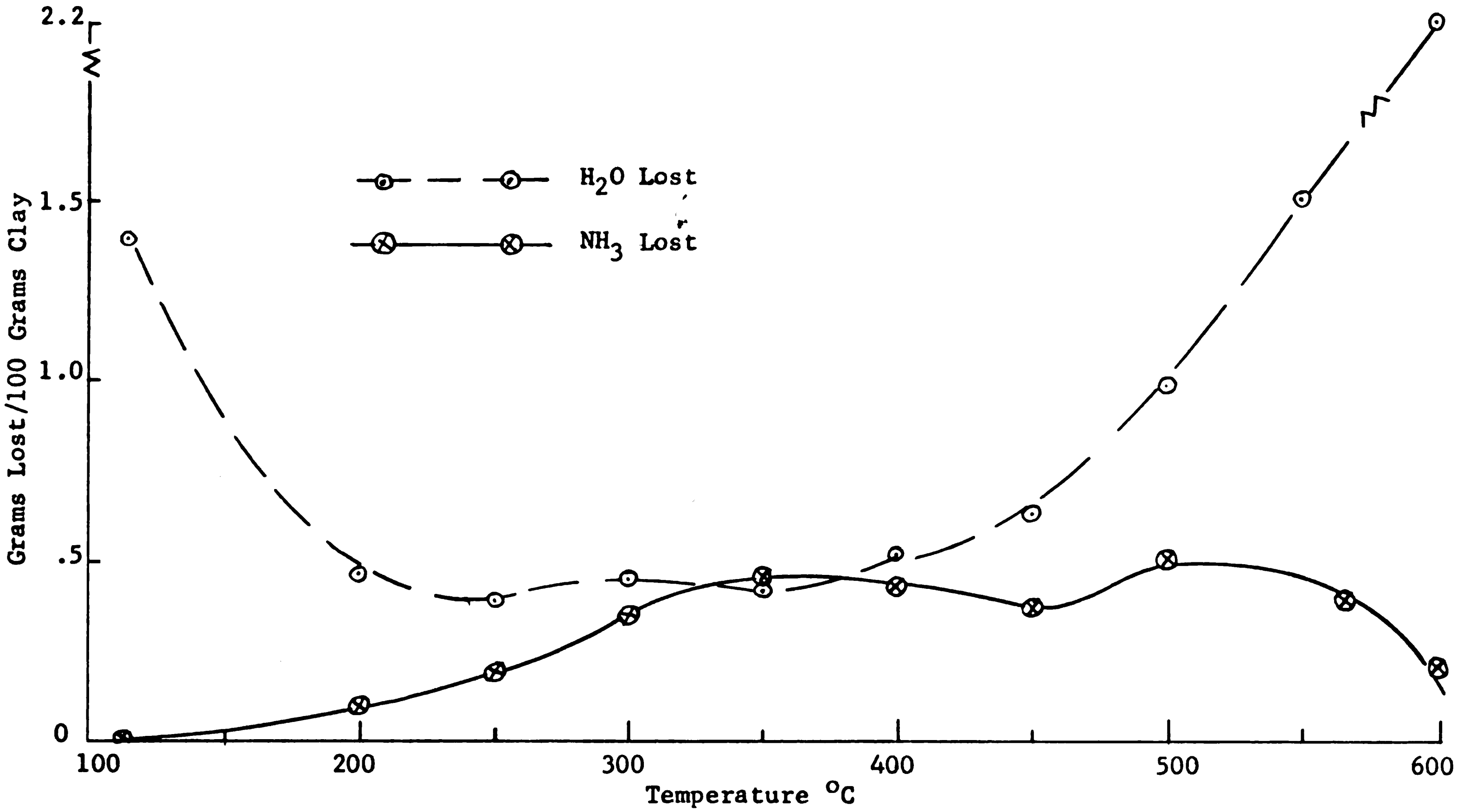

Figure 15. Comparison of the loss of NH_3 and water from bentonite during heating.

represents the loss from 100 grams clay heated over a range of 100 degrees centigrade. Thus, for example, the points at 300 degrees centigrade indicate a loss of 0.36 grams of NH_3 and 0.45 grams of water during the heating interval of 200 to 300 degrees centigrade. The complexity of reactions occurring is well illustrated. Below a temperature of 200 degrees centigrade the entire weight loss may be attributed to loss of water. From 200 to 400 degrees centigrade nearly equal weights of NH_3 and water are lost. Above 400 degrees centigrade increasing amounts of a weight loss which is attributed to dehydroxylation occurs. The exact nature of the water lost between 200 and 400 degrees centigrade has been difficult to explain. MacKenzie (15) suggested that the existence of a bare proton adsorbed on the clay surface would be inconceivable. He postulated that the proton would combine with the hydroxyl group below the hexagonal hole causing a low temperature dehydroxylation. As evidence of this he pointed out that the dehydroxylation endotherm of an NH_3 saturated bentonite was much smaller than that of the natural or sodium saturated bentonite. This was verified as shown in curves 1 and 2, figure 16. However, curve 3 shows that a hydrogen saturated clay also produces a smaller dehydroxylation endotherm. The reduced endotherm could be due to the lower energy reaction when hydrogen ions combine with hydroxyl groups rather than the combination of two hydroxyl groups to produce dehydroxylation.

Table V gives a comparison of weight loss data for a sodium saturated bentonite and an NH_3 saturated bentonite. The NH_3 loss data were taken from Table IV to obtain an estimation of NH_3 lost and to allow calculation of water lost. As can be seen during the

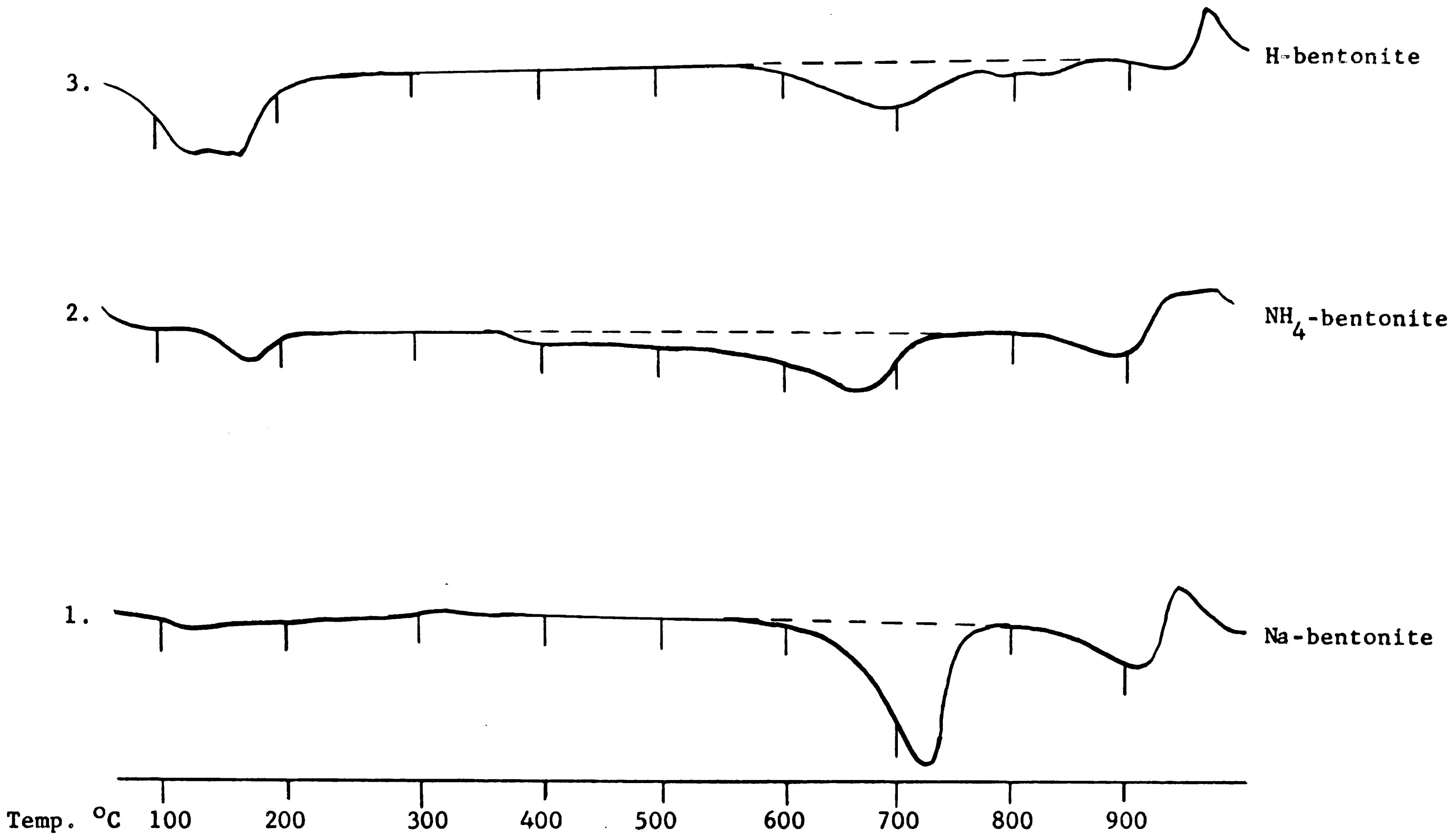

Figure 16. Differential thermal analyses curves of Na-, NH_4-, and H-bentonite; one-sixteenth actual size.

temperature range of 450 to 750 degrees centigrade while dehydroxylation occurs, the water loss is identical from both sodium and NH_4 ion saturated bentonite. This data does not favor MacKenzie's postulate.

TABLE V

A COMPARISON OF THE WEIGHT LOSS DURING DEHYDROXYLATION OF A Na-BENTONITE AND AN NH_4-BENTONITE

Initial Temp. (° C)	Final Temp. (° C)	Time (hrs.)	Na-Bentonite Water Loss (gms/100gms)	NH_4-Bentonite NH_3 Loss (gms/100gms)	NH_4-Bentonite H_2O Loss (gms/100gms)
200	300	24	0.28	0.45	0.62
350	450	24	0.23	0.38	0.77
450	750	18	3.94	0.59	3.90

Barshad (2), studying vermiculite, suggested that the NH_4 ion is closely associated with one water molecule even while on the surface of the clay mineral. He suggested that the energy binding the water and NH_4 ions must be large. If this is true, the ratio of water loss to NH_3 loss should always remain constant. Tables VI and VII give the loss of water and NH_3 from the intermediate aluminum saturated and the aluminum saturated clay respectively. The ratio of water loss to NH_3 loss is greater, approaching two to one in these samples. Thus, it would appear that the water loss may be independent of the NH_3 loss.

One possible explanation is that the water evolves from decomposition of $Al(OH)_3$. The titration curves showed that considerable exchangeable aluminum was present on the clay mineral. When the suspension is neutralized, the aluminum ions may be precipitated

TABLE VI

THE TOTAL WEIGHT, WATER, AND NH_3 LOST FROM BENTONITE WHICH HAD BEEN HYDROGEN SATURATED BY ELECTRODIALYSIS AND THEN NEUTRALIZED WITH NH_4OH

Initial Temp. °C	Final Temp. °C	Time (hrs.)	Total Wt. Lost (gms/100gms)*	Water Content (gms/100gms)*	Water Lost (gms/100gms)*	Dehydroxylation*	NH_3 Content (gms/100gms)*	NH_3 Lost (gms/100gms)*
--	--	--	0.00	1.59	0.00	0.00	1.46	0.00
60	200	10	0.01	1.68	-0.09	0.00	1.36	0.10
200	300	10	0.53	1.42	0.26	0.00	1.09	0.27
300	400	10	0.72	0.99	0.43	0.00	0.80	0.29
400	500	10	1.09	0.53	0.46	0.26	0.43	0.37
500	600	10	3.00	0.06	0.47	2.15	0.05	0.38
--	--	--	0.00	2.35	0.00	0.00	1.20	0.00
60	250	10	0.57	1.86	0.49	0.00	1.12	0.08
250	350	10	0.56	1.49	0.37	0.00	0.93	0.19
350	450	10	0.88	0.90	0.59	0.00	0.64	0.29
450	550	10	1.43	0.12	0.65	0.25	0.11	0.53

*Expressed as grams per 100 grams of water free, NH_3 free bentonite.

TABLE VII

THE TOTAL WEIGHT, WATER, AND NH_3 LOST FROM ALUMINUM SATURATED BENTONITE WHICH HAD BEEN NEUTRALIZED WITH NH_4OH

Initial Temp. °C	Final Temp. °C	Time (hrs.)	Total Wt. Lost (gms/100gms)*	Water Content (gms/100gms)*	Water Lost (gms/100gms)*	Dehydroxylation*	NH_3 Content (gms/100gms)*	NH_3 Lost (gms/100gms)*
--	--	--	0.00	11.64	0.00	0.00	1.32	0.00
60	60	1.5	3.29	8.36	3.28	0.00	1.31	0.01
60	60	1.5	5.23	3.06	5.30	0.00	1.38	-0.07
60	200	10	1.05	2.03	1.03	0.00	1.36	0.02
200	300	10	0.92	1.48	0.55	0.00	0.99	0.37
300	400	10	1.11	0.72	0.76	0.00	0.64	0.35
400	500	10	2.14	0.06	0.66	0.95	0.11	0.53
500	600	10	2.65	0.00	0.06	2.55	0.07	0.04

*Expressed as grams per 100 grams of water free, NH_3 free bentonite.

on the surface of the clay as $Al(OH)_3$. The following reaction may then be postulated for water and NH_3 loss upon heating:

$$\text{Clay} - NH_4 \xrightarrow[\Delta]{} \text{Clay} - H + NH_3$$

$$\text{Clay} \cdot 2Al(OH)_3 \xrightarrow[\Delta]{} \text{Clay} \cdot Al_2O_3 + 3H_2O.$$

The heat of reaction for the second equation as computed from heat of formation data is 15.0 kilocalories per mole of water lost. Thus, for the bentonite clay, which was hydrogen saturated by a resin column and then neutralized with NH_4OH, the heat of reaction should be approximately 35.0 kilocalories for the combined loss of one mole of NH_3 and one mole of water. The fact that the experimental values given in Table III are so close to the theoretical values lends some merit to the postulated mechanism. Colman and Craig (4) have found magnesium as well as aluminum present as exchangeable ions after a hydrogen saturated bentonite has been allowed to stand for a short time. The effects of magnesium have been neglected in this postulate because it is present in much smaller quantities and should decompose below 200 degrees centigrade. It should, however, be noted that this is not positive proof, nor may the mechanism postulated by Barshad be completely ruled out. The increased heat of desorption of NH_3 from the bentonite clay which had been electrodialyzed may readily be explained by the postulated mechanism. As was pointed out previously, the loss of water was greater in the case of the electrodialyzed clays. Two separate samples of bentonite were prepared by electrodialysis. Since the material used for the temperature ranges 250 to 350 and 350 to 450 degrees centigrade does not hold as much NH_3 as the other preparation, it would appear that it has undergone more decomposition and would, therefore, be expected to contain more exchangeable aluminum. In this sample, nearly two moles of water were lost for each mole of NH_3 lost which accounts for the higher heats of reaction. No attempt was made to calculate heats of reactions for temperature ranges other than from 200 to 450 degrees centigrade because of the lack of a well defined reaction except in this temperature range.

Curve 1, figure 17 shows the differential thermal analysis curve of aluminum saturated bentonite. The exothermic peak near 550 degrees centigrade indicates the presence of an impurity. Since difficulty was encountered with flocculation of the clay and separation of the clay from the resin during the preparation of an aluminum saturated bentonite, it is reasonable to assume that some of the Amberlite resin was carried with the flocculated clay. The use of the nitrogen pretreatment was apparently effective in eliminating this exothermic reaction as shown in curve 2, figure 17; however, there appeared to be changes in the size of the endothermic dehydroxylation peak upon heating. This may be seen in curves 3 and 4 of figure 17. It should also be noted that between 300 and 500 degrees no increase was noted in the dehydroxylation endotherm. Therefore, a value for the heat of desorption of NH_3 for the temperature range 300 to 400 degrees centigrade was the only value calculated. The value obtained was 61.2 kilocalories per mole of NH_3 lost. Because of the impurity contained in this sample, little confidence can be placed in the reliability of this value.

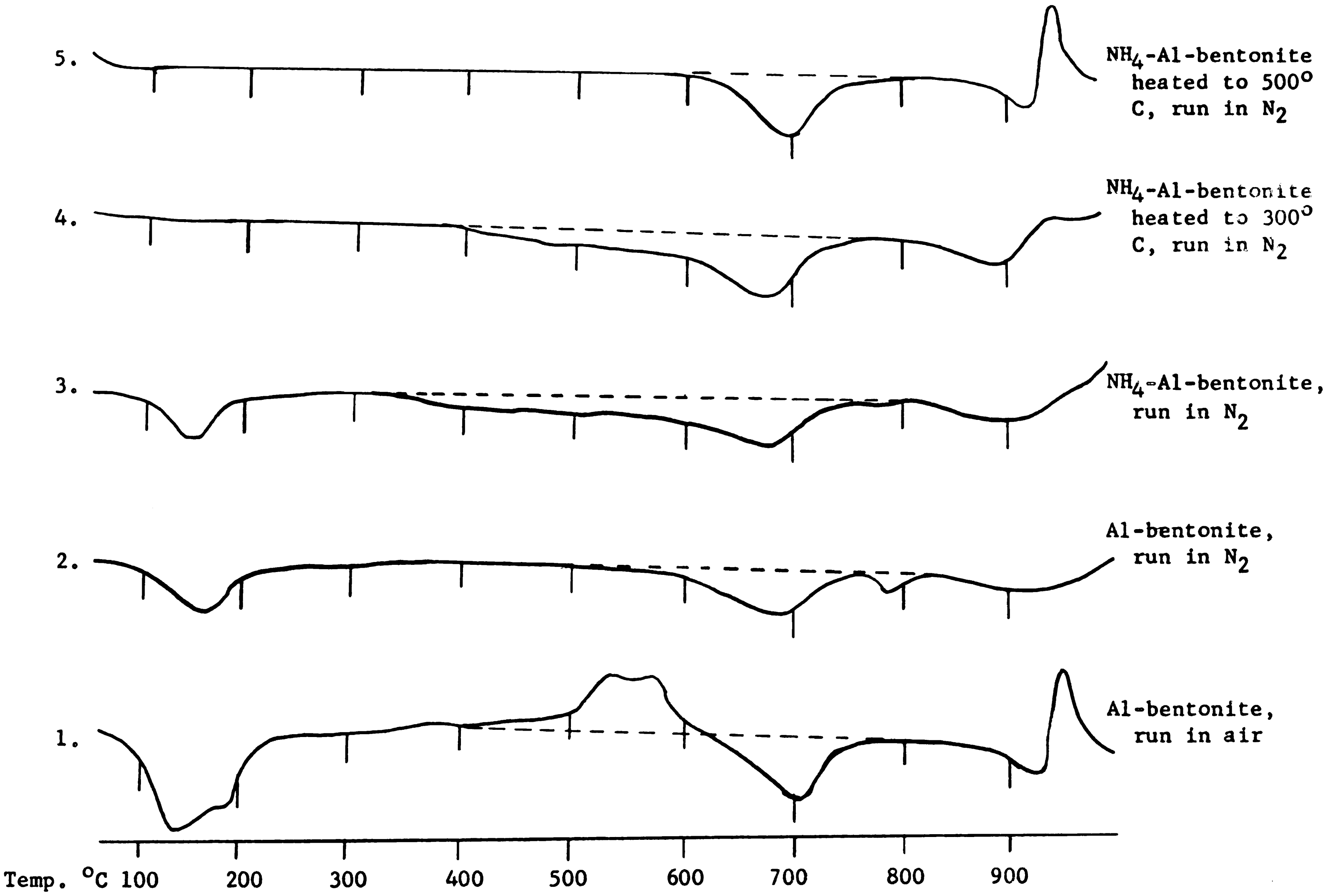

Figure 17. Differential thermal analyses curves of Al^{+++} and NH_4-Al saturated bentonite; one-sixteenth actual size.

Differential Thermal Analysis of Methylamine and Ethylamine Saturated Bentonite

When an amine such as methylamine or ethylamine is added to an acid system, it readily forms the positive charged cation, $R\text{-}NH_3^+$. It would then appear that the cation form of the amine should be held as an exchangeable cation by bentonite. Differential thermal analyses curves 1 in figure 18 and 1 in figure 19 show that large exothermic reactions occur upon heating the methylamine and ethylamine saturated bentonite in air. However, if the same material is run in a nitrogen atmosphere, the resulting curves, shown in figures 18 and 19, are very similar to the curves for NH_3 loss discussed in the prior section.

The heats of reaction for loss of methylamine and ethylamine were determined by the same procedure used for the NH_3 saturated bentonite. The heats of reaction are given in Table VIII.

TABLE VIII

THE HEATS OF REACTION OF METHYLAMINE AND ETHYLAMINE RELEASED FROM BENTONITE

Temperature Range ° C	Methylamine-Bentonite ΔH (K Cal/mole)*	Ethylamine-Bentonite ΔH (K Cal/mole)*
200-300	38.5	196.0
300-400	40.3	164.0
250-350	42.1	252.0
350-450	42.6	16.1

*Expressed as kilocalories per mole of amine released.

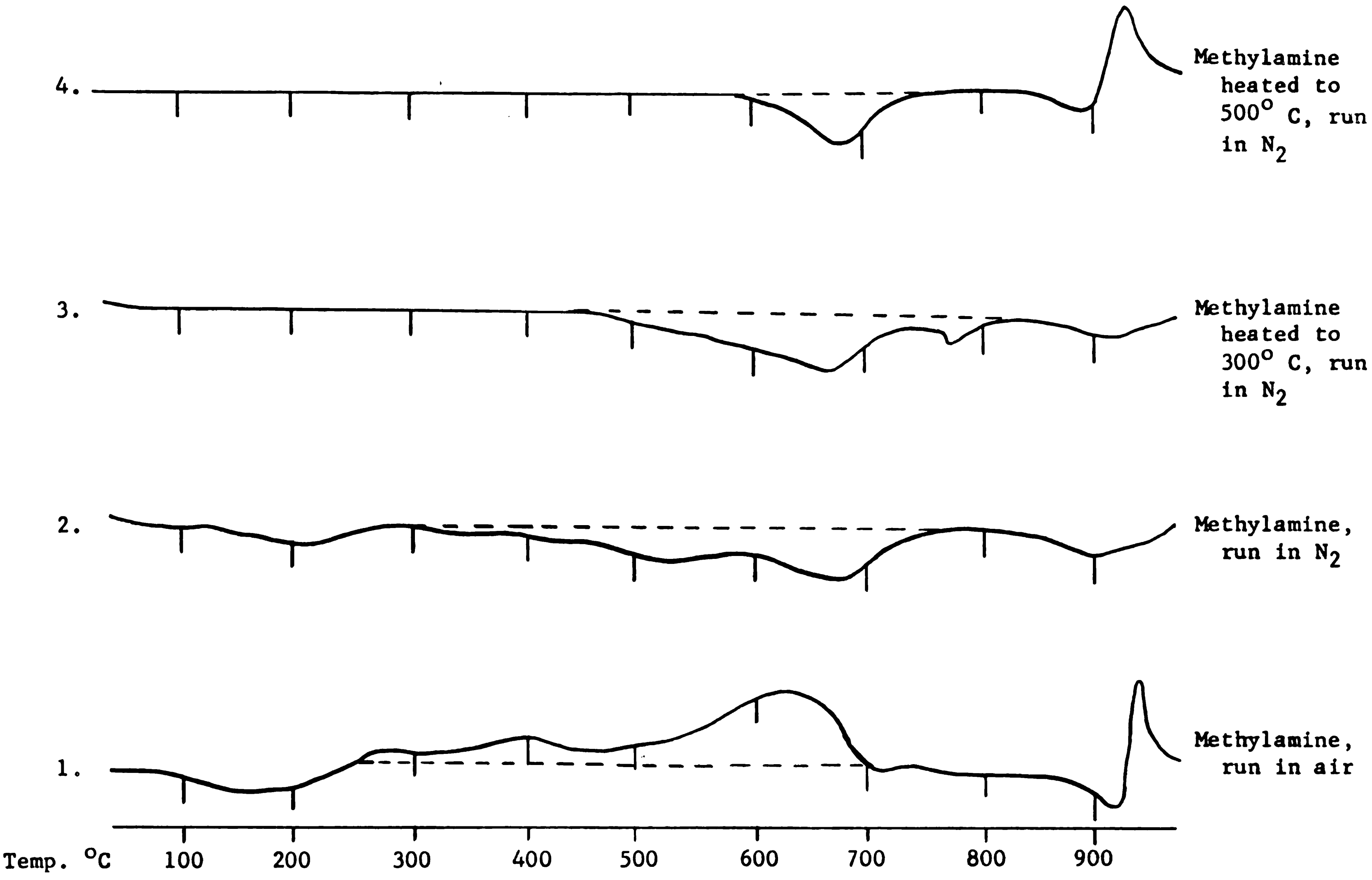

Figure 18. Differential thermal analyses curves of methylamine saturated bentonite; one-sixteenth actual size.

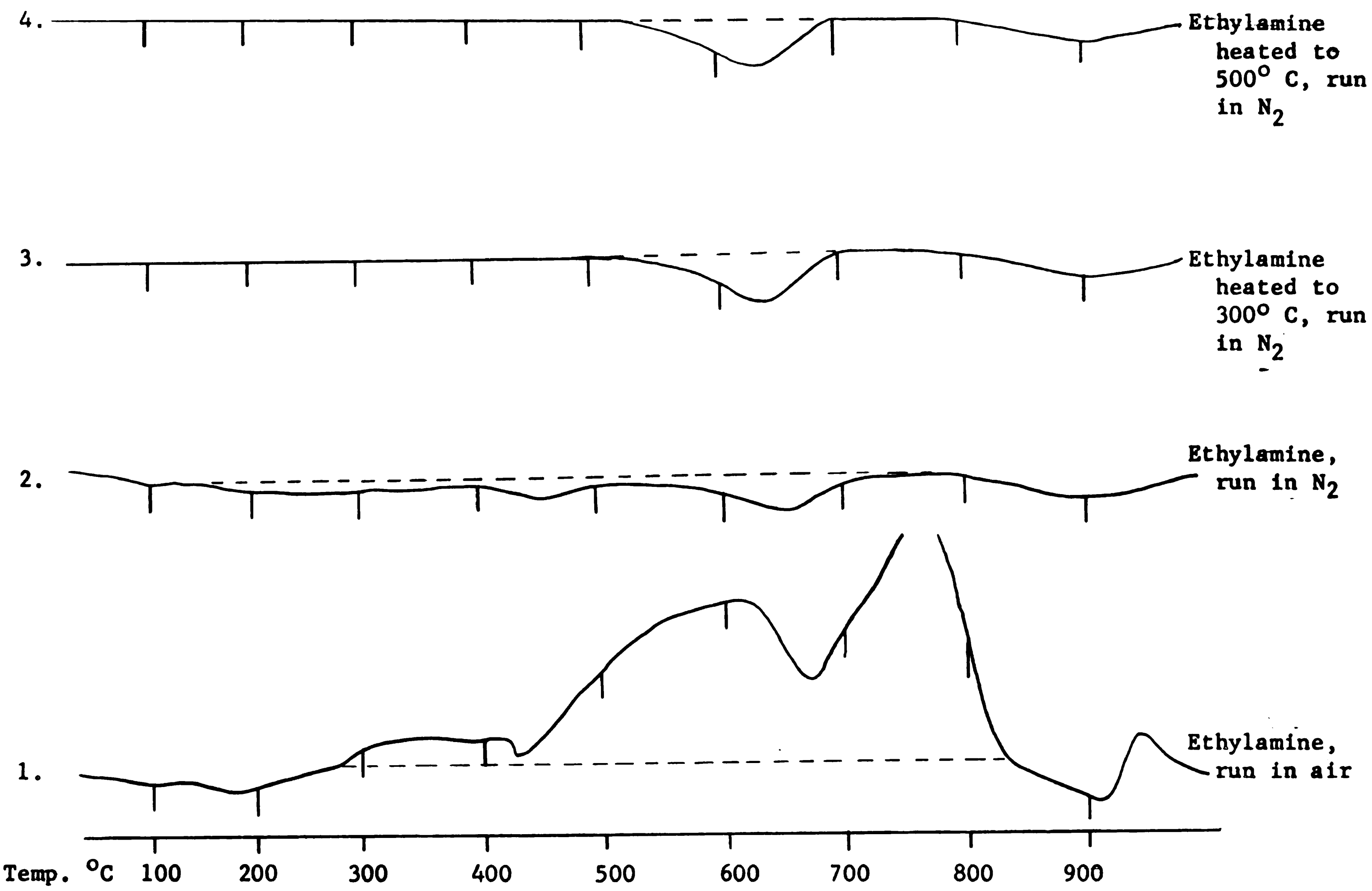

Figure 19. Differential thermal analyses curves of ethylamine saturated bentonite; one-sixteenth actual size.

The heats of reaction of methylamine are very similar to those obtained for release of NH_3 from bentonite. Examination of the weight loss data in Table IX shows that the loss of one mole of methylamine is again accompanied by the loss of one mole of water. It should also be noted that a methylamine saturated bentonite dried at 60 degrees centigrade under vacuum contained 4.15 grams or 129 milliequivalents methylamine per 100 grams bentonite. This is approximately 40 milliequivalents greater than the cation exchange capacity. Twenty milliequivalents of the methylamine were lost upon heating the sample to 200 degrees centigrade and the sample heated to 250 degrees centigrade contained 91 milliequivalents of methylamine, approximately the cation exchange capacity of the bentonite. The rapid loss of this excess methylamine suggests that it was held by weak physical forces, although the concurrent loss of an unknown quantity of water in this region makes it impossible to estimate the energy associated with these physical forces. The average ΔH for the loss of methylamine from 200 to 450 degrees centigrade is 40.9 kilocalories per mole lost as compared to 35.3 kilocalories per mole of NH_3 lost during the same temperature region from the bentonite containing the least exchangeable aluminum.

The heats of reaction obtained for loss of ethylamine from bentonite given in Table VIII are extremely large except for the 350 to 450 degree centigrade range. This very low value is attributed to experimental error. It may also be noted in Table X that the loss of extremely large quantities of water occurred up to 400 degrees centigrade. For example, in the range 300 to 400 degrees centigrade for each mole of ethylamine lost approximately seventeen

TABLE IX

THE TOTAL WEIGHT, WATER, AND METHYLAMINE LOST FROM METHYLAMINE SATURATED BENTONITE

Initial Temp. °C	Final Temp. °C	Time (hrs.)	Total Wt. Lost (gms/100gms)*	Water Content (gms/100gms)*	Water Lost (gms/100gms)*	Dehydroxylation*	CNH_5 Content (gms/100gms)*	CNH_5 Lost (gms/100gms)*
60	& Vacuum	--	0.00	3.10	0.00	0.00	4.07	0.00
60	200	10	1.65	2.02	1.08	0.00	3.50	0.57
200	300	10	2.33	1.14	0.88	0.00	2.05	1.45
300	400	10	0.94	0.81	0.33	0.00	1.44	0.61
400	500	10	2.96	0.09	0.72	0.96	0.16	1.28
500	600	10	1.55	0.00	0.09	1.30	0.00	0.16
60	& Vacuum	--	0.00	7.20	0.00	0.00	4.23	0.00
60	250	10	6.82	1.68	5.52	0.00	2.93	1.30
250	350	10	1.67	0.98	0.70	0.00	1.96	0.97
350	450	10	2.45	0.32	0.66	0.62	0.79	1.17
450	550	10	4.42	0.00	0.32	3.52	0.21	0.58

*Expressed as grams per 100 grams of water free, CNH_5 free bentonite.

TABLE X

THE TOTAL WEIGHT, WATER, AND ETHYLAMINE LOST FROM ETHYLAMINE SATURATED BENTONITE

Initial Temp. °C	Final Temp. °C	Time (hrs.)	Total Wt. Lost (gms/100gms)*	Water Content (gms/100gms)*	Water Lost (gms/100gms)*	Dehydro-xylation*	C_2NH_7 Content (gms/100gms)*	C_2NH_7 Lost (gms/100gms)*
60	& Vacuum	--	0.00	8.52	0.00	0.00	7.73	0.00
60	200	10	3.80	7.96	0.56	0.00	4.49	3.24
200	300	10	6.71	2.78	5.18	0.00	2.96	1.53
300	400	10	2.26	0.81	1.97	0.00	2.67	0.29
400	600	10	7.60	0.00	0.81	4.70	0.58	2.09
60	& Vacuum	--	0.00	7.62	0.00	0.00	7.41	0.00
60	250	10	6.70	3.81	3.81	0.00	4.52	2.89
250	350	10	3.09	1.08	2.73	0.00	4.16	0.36
350	450	10	2.93	0.52	0.56	0.00	1.79	2.37
450	550	10	6.06	0.00	0.52	4.22	0.47	1.32

*Expressed as grams per 100 grams of water free, C_2NH_7 free bentonite.

moles of water were lost. This might indicate that considerable water of hydration is associated with ethylamine. The heat of solution at infinite dilution as given by the International Critical table is 6.33 kilocalories per mole of ethylamine. This would not indicate that a large energy should be expected from dehydration of ethylamine. However, Walker reported that butylamine and water were capable of expanding vermiculite to basal spacings greater than 500 angstroms. He suggested that the butylamine and water form an "iceberg" type structure.[1] If such a relationship exists with ethylamine, water, and montmorillonite, it would readily explain the large water losses and high energies of desorption of ethylamine from bentonite.

Differential Thermal Analysis of Organic Acid and Alcohol Saturated Bentonite

Differential thermal analyses curves of methanol and ethanol treated bentonite are shown in figure 20. Some of the alcohols were adsorbed by the bentonite as evidenced by the exothermic peak when the samples were run in air. However, once oxidation was suppressed in the sample by use of nitrogen gas, little evidence of a bonding energy is shown. It would appear that they are weakly bonded and the bond energy not detectible by differential thermal analysis even though some of the alcohols were present on the clay.

Formic acid and acetic acid gave results very similar to the alcohols. Evidence of the presence of the organic acid is given by the exothermic peaks in curves 1 and 3 in figure 21.

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[1] George F. Walker, Technical paper presented at the Ninth Annual Clay Minerals Conference, October, 1960.

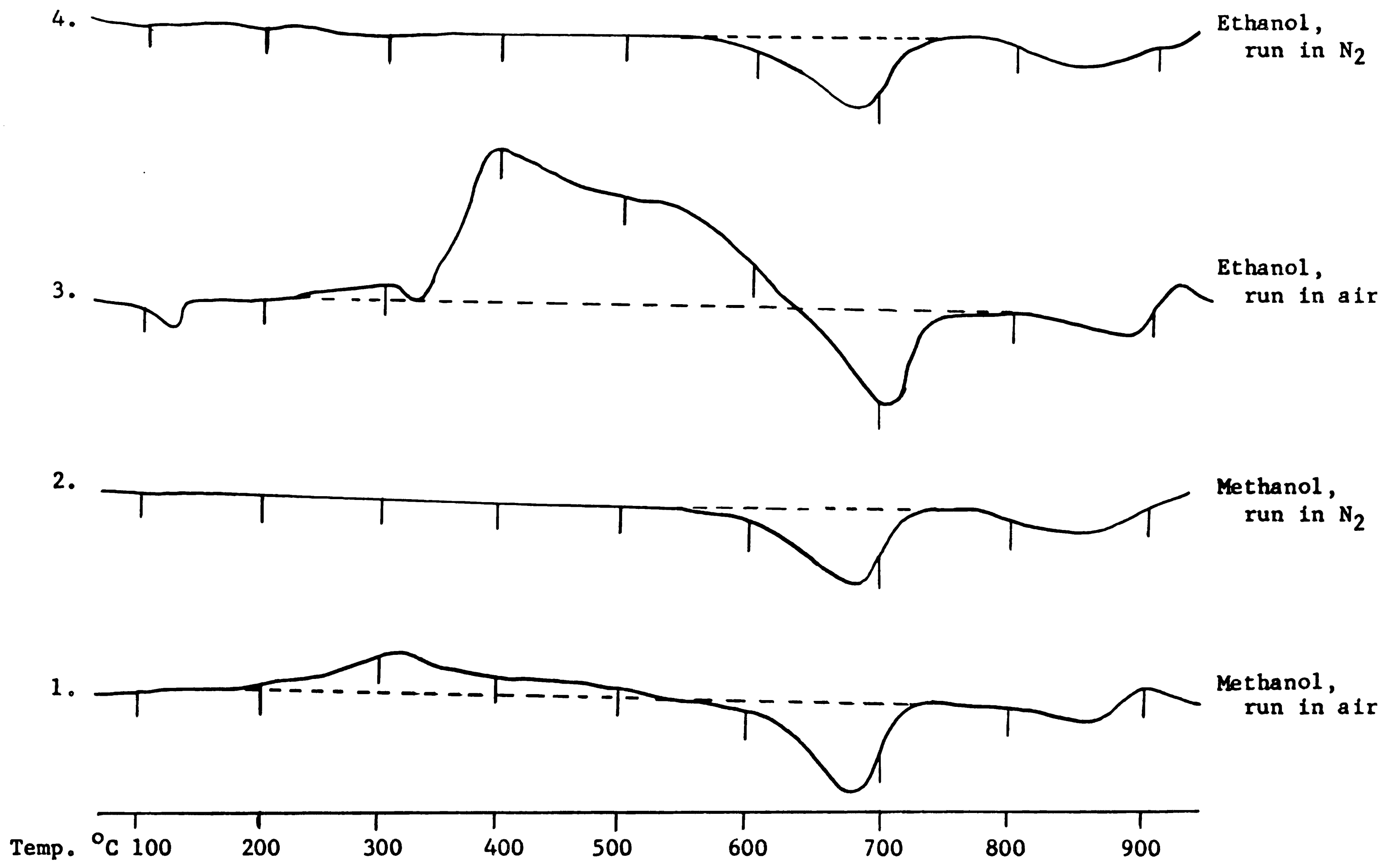

Figure 20. Differential thermal analyses curves of methanol and ethanol saturated bentonite; one-sixteenth actual size.

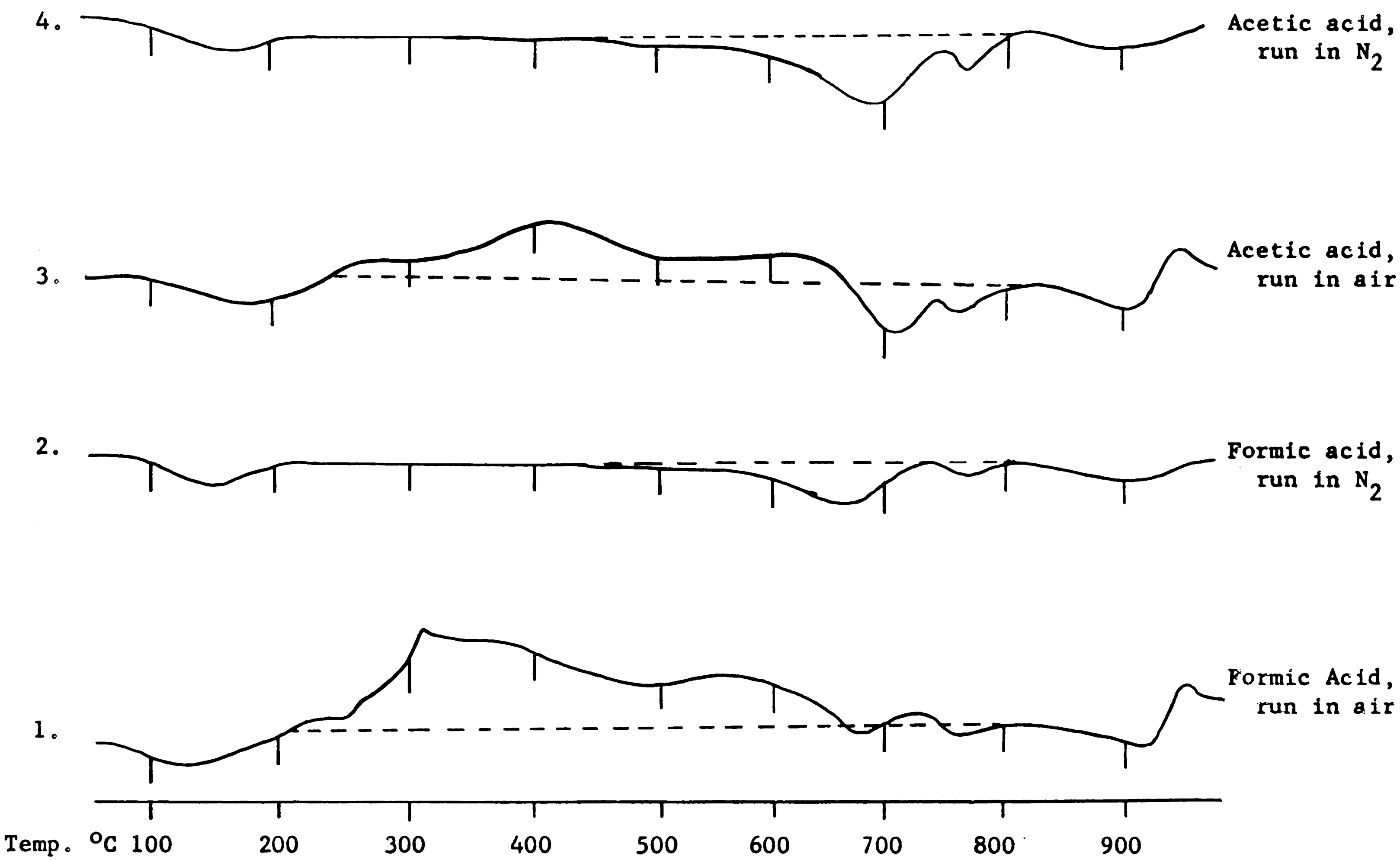

Figure 21. Differential thermal analyses curves of formic and acetic acid saturated bentonite; one-sixteenth actual size.

However, once again when oxidation was eliminated, little evidence of bonding energy is shown. It is interesting to note that the endotherm is smaller for curves 2 and 4, figure 21, for the organic acid saturated bentonite than for the corresponding curves of alcohol saturated bentonite shown in figure 20. This again gives evidence that the presence of hydrogen ions results in a lower energy dehydroxylation.

General Discussion of Heat of Reaction Data

No discussion of heat of reaction data would be complete without generalizations as to its applicability and some estimate of the errors involved in its measurements. To illustrate the errors involved in estimation of the heats of reaction of NH_3 desorption by differential thermal analysis, an example will be used. An estimate of the errors in determinations for the NH_4-bentonite with least exchangeable aluminum heated from 200 to 300 degrees centigrade is given in Table XI. Two sources of error not listed in Table XI exist which are difficult to estimate. First, the reliability of the standard curve is open to some question. However, if the base line is accurately established, it appears that this error should be less than two per cent. The second error comes from the effect of a temperature on the heat of reaction. It is well known that $\Delta H = \Delta H_0 + \int_{t_1}^{t_2} \Delta Cpdt$. Since the heat of reaction used in the calibration curves were all for 298 degrees centigrade, an error undoubtedly occurs because of the effect of temperature on heat capacity. However, it would appear that both of the above errors are small in comparison to the error in determining the change in nitrogen content and the change in area. This example readily points out that when measurements are based on small differences, rather large errors may result. The nitrogen determinations were made in duplicate and the areas were determined in duplicate which should reduce the probability of attaining the maximum error.

TABLE XI

ESTIMATION OF ERRORS IN DETERMINATION OF HEATS OF REACTION

Determination	Quantity	Estimated Error	Estimated % Error
1. Total Wt. Loss	0.7449 gms.	± 0.0002 gms.	0.03
2.(a) Total Nitrogen 200° C	81.6 m.e./100g.	± 0.8 m.e./100g.	1.0
(b) Total Nitrogen 300° C	60.6 m.e./100g.	± 0.6 m.e./100g.	1.0
(c) Nitrogen Lost	21.0 m.e./100g.	± 1.4 m.e./100g.	7.0
3. Water Lost	0.45 gm/100g.	± 0.02 gms.	4.0
4.(a) Weight of Area 200° C	0.728 gms.	± 0.007 gms.	1.0
(b) Weight of Area 300° C	0.642 gms.	± 0.006 gms.	1.0
(c) Change in Area	0.086 gms.	± 0.013 gms.	15.0

While the heats measured are from the heat absorbed when a bond is broken, it must not be assumed that this is the energy involved in the release of the ion in the soil. In a natural soil system the energy involved is that of exchange of one ion for another, for example, the exchange of hydrogen ions for NH_4 ions. The net energy change for cation exchange in soils would not be the same as the energy change when NH_4 ions decompose to form NH_3 and hydrogen ions.

CHAPTER V

DIFFERENTIAL THERMAL STUDIES OF VERMICULITE

Differential thermal curves of vermiculite tend to be quite variable. Barshad (2) found differential thermal curves which range from vermiculite with little or no heat changes occurring until 800 degrees centigrade to material which exhibited rather strong dehydroxylation peaks near 500 degrees centigrade. In studying the nature of an NH_3 saturated vermiculite he obtained differential thermal curves which gave no sharp peaks, but produced small, broad exothermic peaks. He studied the loss of NH_3 and water from vermiculite and drew the following conclusions:

> (a) The loss in weight up to a temperature of 255° C. is of water alone,
>
> (b) the loss between 255° C. - 550° C. is relatively small and consists of equal amounts of NH_3 and H_2O in terms of equivalents,
>
> (c) the loss between 550° C. - 600° C. is considerable and also consists of equivalent amounts of NH_3 and H_2O, and
>
> (d) between 600° C. - 800° C. the loss consists of water alone and is equal to crystal lattice water, i.e. OH^- of the octahedral layer.[1]

Scott, et al. (25) found that exchangeable NH_4 ions were decomposed by heating at 400 degrees centigrade while NH_4 ions

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[1] Issac Barshad, "Vermiculite and Its Relation to Biotite," American Mineralogist, 33:669, 1948.

fixed on vermiculite were stable until nearly 400 degrees centigrade and then required heat at 600 degrees centigrade for 24 hours for complete removal of fixed NH_4 ions.

The experimental methods used for studying the heats of desorption of NH_3, methylamine, and ethylamine from vermiculite were the same as those described in Chapter IV for bentonite. Differential thermal analyses curves for NH_4-bentonite are given in figure 22. As can be seen from curve 2, the loss of NH_3 did not yield sharp, well defined peaks. It should also be pointed out that the base line was not the same as that obtained by comparing Al_2O_3 against Al_2O_3. This drift of the base line in the differential thermal analyses curves is associated with changing thermal properties, i.e. thermal diffusivity and/or heat capacity of the sample, upon heating. From a theoretical point of view a simple relationship between peak area and heat of reaction would no longer be expected and the use of a calibration curve to obtain heats of reaction is very questionable. Furthermore, the drift of a base line makes it impossible to establish the new base line with any degree of accuracy.

The heats of reaction estimated for desorption of NH_3 from vermiculite are given in Table XII. It can be seen that the values calculated are quite variable. Part of the variability would appear to be accounted for by the simultaneous loss of water. The weight loss data given in Table XIII shows that below 350 degrees centigrade the entire loss may be attributed to water. It may also be seen that the larger ΔH of desorption values are associated with large water losses. However, there appears to be more

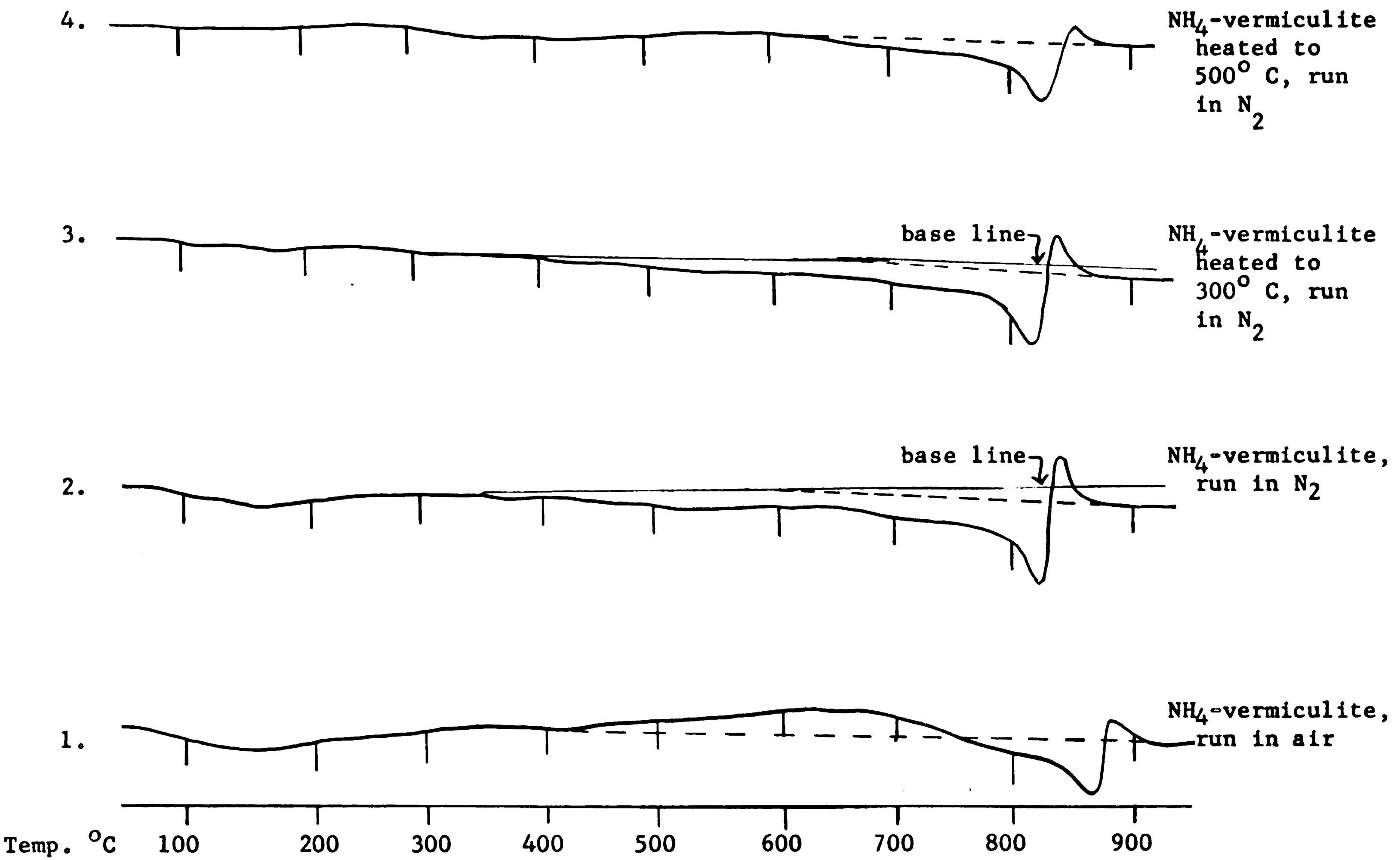

Figure 22. Differential thermal analyses curves of NH_3 saturated vermiculite; one-sixteenth actual size.

variability than can be accounted for by water loss. It is felt that large experimental errors have resulted from difficulties in correctly establishing the base line.

TABLE XII

THE HEAT OF REACTION OF NH_3 RELEASED FROM NH_3 SATURATED VERMICULITE*

Initial Temp. °C	Final Temp. °C	ΔH K Cal/mole NH_3**
300	400	96.4
400	500	120.9
500	600	18.3
350	450	29.8
450	550	55.2
550	650	91.5

*Values for temperature ranges 300-400, 400-500, and 500-600 are from one sample while values for the temperature ranges 350-450, 450-550, and 550-650 are from another sample preparation.

**Expressed as kilocalories per mole of NH_3 evolved.

Differential thermal analyses curves of methylamine and ethylamine saturated vermiculite are shown in figures 23 and 24 respectively. The curves obtained by making analyses under nitrogen gas are very similar to those obtained from NH_3 saturated vermiculite. The base line again drifted during the determination. The estimated heats of desorption for methylamine and ethylamine from vermiculite are given in Tables XIV and XV. Again a large variability is found. The weight loss data given in Table XVI

TABLE XIII

THE TOTAL WEIGHT, WATER, AND NH_3 LOST FROM NH_3 SATURATED VERMICULITE

Initial Temp. °C	Final Temp. °C	Time (hrs.)	Total Wt. Lost (gms/100gms)*	Water Content (gms/100gms)*	Water Lost (gms/100gms)*	NH_3 Content (gms/100gms)*	NH_3 Lost (gms/100gms)*
60	& Vacuum	--	0.00	7.65	0.00	1.05	0.00
60	200	10	4.59	3.15	4.50	0.96	0.09
200	300	10	1.23	1.95	1.20	0.93	0.03
300	400	10	0.61	1.49	0.46	0.78	0.15
400	500	10	1.78	0.10	1.39	0.39	0.39
500	600	10	0.48	0.00	0.10	0.01	0.38
60	& Vacuum	--	0.00	11.27	0.00	1.15	0.00
60	250	10	6.14	5.14	6.13	1.14	0.01
250	350	10	3.33	1.75	3.39	1.20	-0.06
350	450	10	0.80	1.48	0.27	0.67	0.53
450	550	10	1.98	0.02	1.46	0.15	0.52
550	650	10	0.15	0.00	0.02	0.02	0.13

*Expressed as grams per 100 grams of NH_3 free, water free vermiculite.

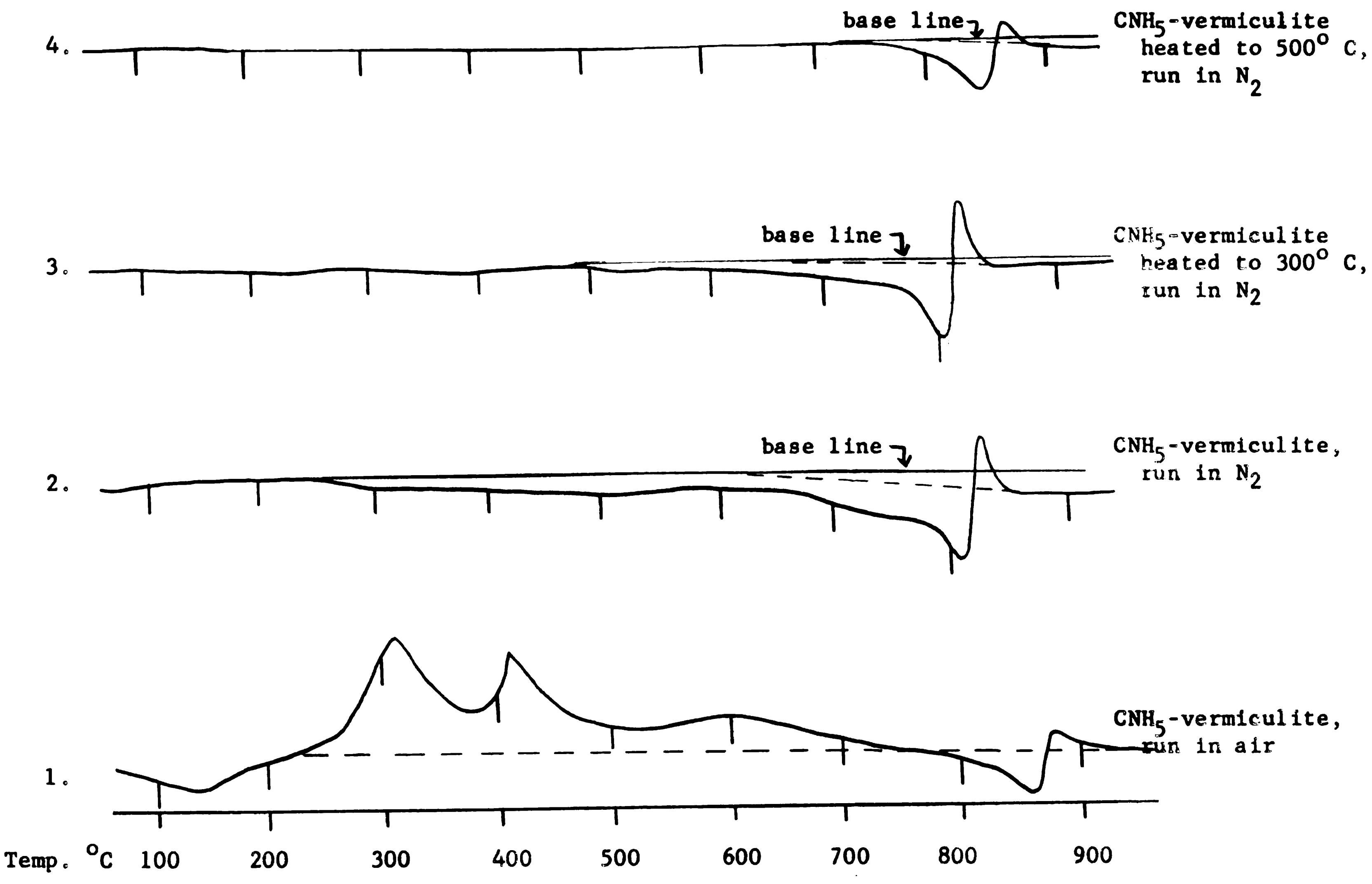

Figure 23. Differential thermal analyses curves of methylamine saturated vermiculite; one-sixteenth actual size.

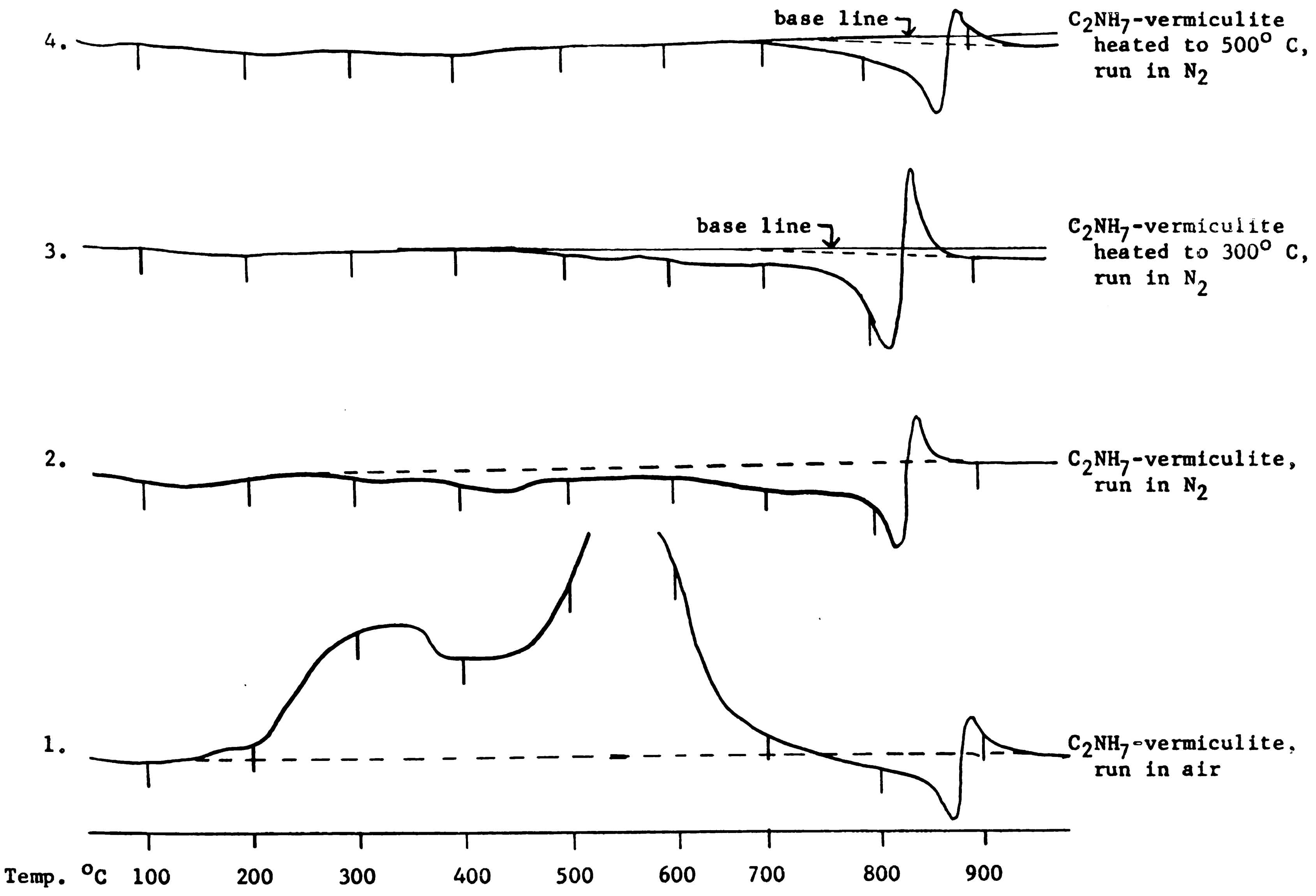

Figure 24. Differential thermal analyses curves of ethylamine saturated vermiculite; one-sixteenth actual size.

shows that relatively little loss of methylamine occurs below 200 degrees centigrade. However, the loss of methylamine begins at a lower temperature than did the loss of NH_3. It may be seen in Table XVII that more than twice as many equivalents of ethylamine are held by the vermiculite than either methylamine or NH_3. However, some of the ethylamine is driven off by heating the sample to 200 degrees centigrade and much more is removed by heating the sample to 300 degrees centigrade. However, the largest losses occur between 250 and 450 degrees centigrade.

TABLE XIV

THE HEAT OF REACTION OF METHYLAMINE RELEASED FROM METHYLAMINE SATURATED VERMICULITE*

Initial Temp. °C	Final Temp. °C	ΔH K Cal/mole CNH_5**
200	300	266
300	400	150
400	500	47
250	350	230
350	450	22
450	550	52

*Values for the temperature ranges 200-300, 300-400, and 400-500 are from one sample while values for the temperature ranges 250-350, 350-450, and 450-550 are from another sample preparation.

**Expressed as kilocalories per mole of CNH_5 evolved.

It should again be pointed out that the estimated heats of reaction involving vermiculite cannot be considered valid because of the change in thermal properties of the sample upon heating.

TABLE XV

THE HEAT OF REACTION OF ETHYLAMINE RELEASED FROM ETHYLAMINE SATURATED VERMICULITE*

Initial Temp. °C	Final Temp. °C	ΔH K Cal/mole C_2NH_7**
200	300	62
300	400	32
400	500	58
500	600	21
250	450	27
450	550	49

*Values for the temperature ranges 200-300, 300-400, 400-500, and 500-600 are from one sample while values for the temperature ranges 250-450 and 450-550 are from another sample preparation.

**Expressed as kilocalories per mole of C_2NH_7 evolved.

TABLE XVI

THE TOTAL WEIGHT, WATER, AND METHYLAMINE LOST FROM METHYLAMINE SATURATED VERMICULITE

Initial Temp. °C	Final Temp. °C	Time (hrs.)	Total Wt. Lost (gms/100gms)*	Water Content (gms/100gms)*	Water Lost (gms/100gms)*	CNH_5 Content (gms/100gms)*	CNH_5 Lost (gms/100gms)*
60	& Vacuum	--	0.00	5.86	0.00	2.38	0.00
60	200	10	4.24	1.63	4.23	2.37	0.01
200	300	10	1.99	0.33	1.30	1.68	0.69
300	400	10	0.71	-0.13	0.46	1.43	0.25
400	500	10	0.64	-0.01	-0.12	0.67	0.76
500	600	10	0.66	0.00	-0.01	0.00	0.67
60	& Vacuum	--	0.00	5.95	0.00	2.47	0.00
60	250	10	5.96	0.66	5.29	1.80	0.67
250	350	10	0.30	0.60	0.06	1.56	0.24
350	450	10	0.85	0.30	0.30	1.01	0.55
450	550	10	1.31	0.00	0.30	0.00	1.01

*Expressed as grams per 100 grams of methylamine free, water free vermiculite.

TABLE XVII

THE TOTAL WEIGHT, WATER, AND ETHYLAMINE LOST FROM ETHYLAMINE SATURATED VERMICULITE

Initial Temp. °C	Final Temp. °C	Time (hrs.)	Total Wt. Lost (gms/100gms)*	Water Content (gms/100gms)*	Water Lost (gms/100gms)*	C_2NH_7 Content (gms/100gms)*	C_2NH_7 Lost (gms/100gms)*
60	& Vacuum	--	0.00	7.90	0.00	7.34	0.00
60	200	10	4.92	3.87	4.03	6.45	0.89
200	300	10	3.05	1.59	2.28	5.68	0.77
300	400	10	5.23	0.23	1.36	1.81	3.87
400	500	10	0.90	0.26	-0.03	0.88	0.93
500	600	10	1.05	0.00	0.26	0.09	0.79
60	& Vacuum	--	0.00	10.34	0.00	7.57	0.00
60	250	10	10.08	2.43	7.91	5.40	2.17
250	350	10	2.65	1.40	1.03	3.78	1.62
350	450	10	2.07	0.97	0.43	2.14	1.64
450	550	10	1.78	0.95	0.02	0.38	1.76
550	650	10	1.33	0.00	0.95	0.00	0.38

*Expressed as grams per 100 grams of ethylamine free, water free vermiculite.

CHAPTER VI

DIFFERENTIAL THERMAL ANALYSIS OF SOILS HIGH IN ORGANIC MATTER

Differential thermal analyses of some soil clays have been difficult to interpret because of the presence of organic materials. Wurman (37) reported large exotherms at temperatures as high as 750 degrees centigrade from the clay fraction of a Wallace sand. These large exotherms tend to mask the reactions occurring in the soil clays.

The success of the use of nitrogen gas to prevent oxidation of NH_3 suggests that it might be used to prevent oxidation of organic matter in soil samples and thus allow for better interpretation of differential thermal analyses curves. Mitchell and MacKenzie (18) have described a method using nitrogen gas with which they were able to supress oxidation in soil samples.

To test the possibility of studying soil samples by the use of controlled nitrogen atmospheres while making differential thermal analyses, a profile sample of Blue Lake sand[1], similar to the Wallace sand, was selected for study. The following sample preparations were used for each horizon: (1) entire soil, (2) less than

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[1] Profile sample and classification of Blue Lake sand, courtesy of Donald F. Franzmeier.

two micron fraction, organic matter not destroyed, and (3) less than two micron fraction, treated with H_2O_2 to destroy organic matter. Each of the samples were run in air and under nitrogen gas.

It may readily be seen in figures 25, 26, and 27 that oxidation has been stopped by use of a nitrogen atmosphere. The differential thermal curves for the entire soil show that large quantities of organic matter are present in the A_1 horizon which tends to mask the quartz peak at 575 degrees centigrade. However, curve 2 shows that the use of nitrogen gas eliminates oxidation and yields the characteristic quartz peak. This is not surprising for a sand soil.

The other two horizons of the soil are quite low in organic matter; thus, the use of a controlled atmosphere is of little advantage.

In comparing figures 26 and 27 it may be observed that essentially the same differential thermal analysis curve is obtained for the less than two micron fraction of B_h and B_t horizon without destroying organic matter and using a nitrogen atmosphere as is obtained by destroying the organic matter with H_2O_2. It may also be noted in figure 27 that some organic matter remained even after treatment with H_2O_2; therefore, it may be concluded that differential thermal analysis of the clay fraction under nitrogen atmosphere without destroying the organic matter is superior to analysis in air after the sample has been treated with H_2O_2.

The A_1 horizon showed less favorable results. The differential thermal analyses curves showed little deviation from the base line. This is undoubtedly due to the high per cent of organic matter in

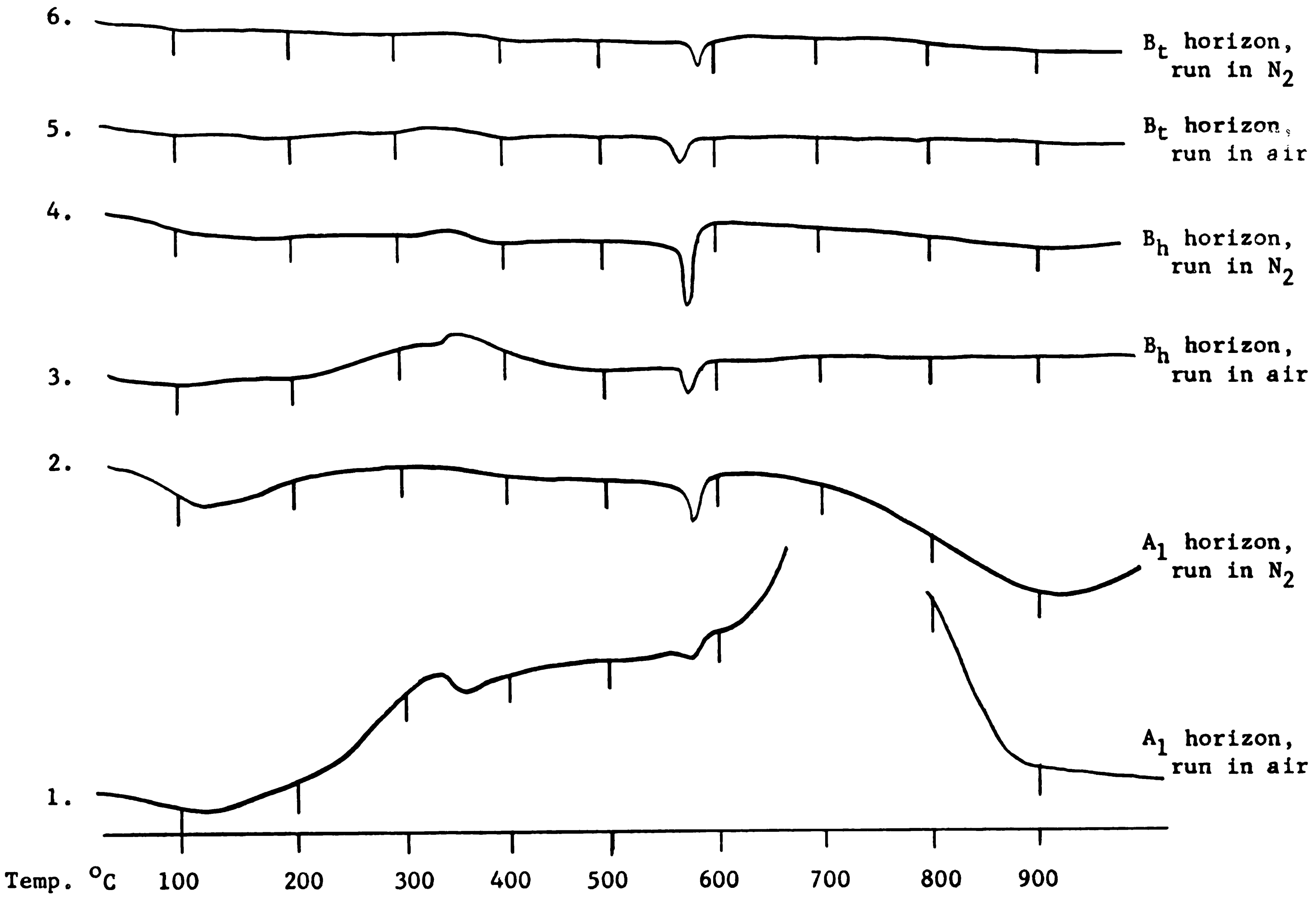

Figure 25. Differential thermal analyses curves of Blue Lake sand.

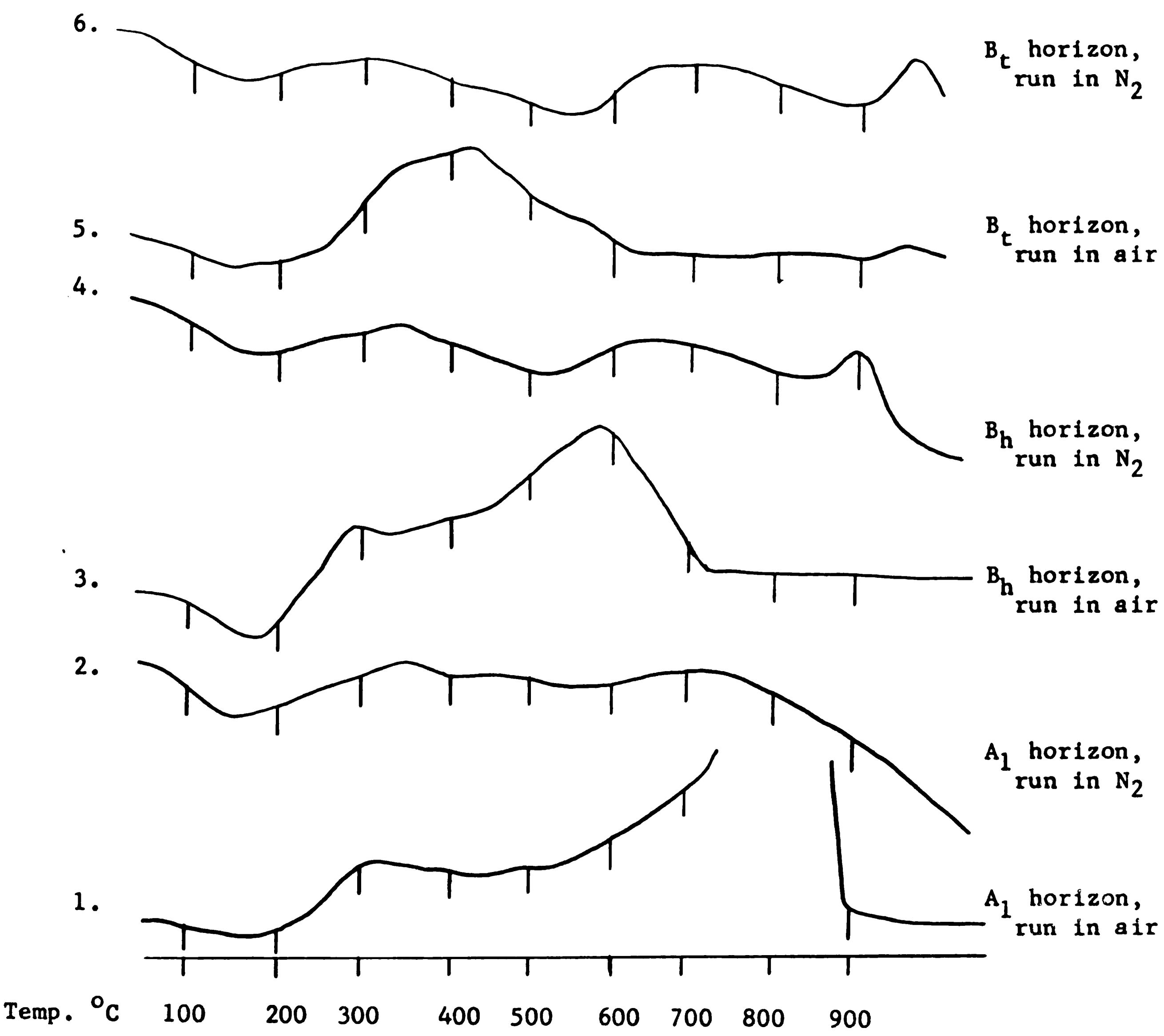

Figure 26. Differential thermal analyses curves of the less than two micron fraction of Blue Lake sand.

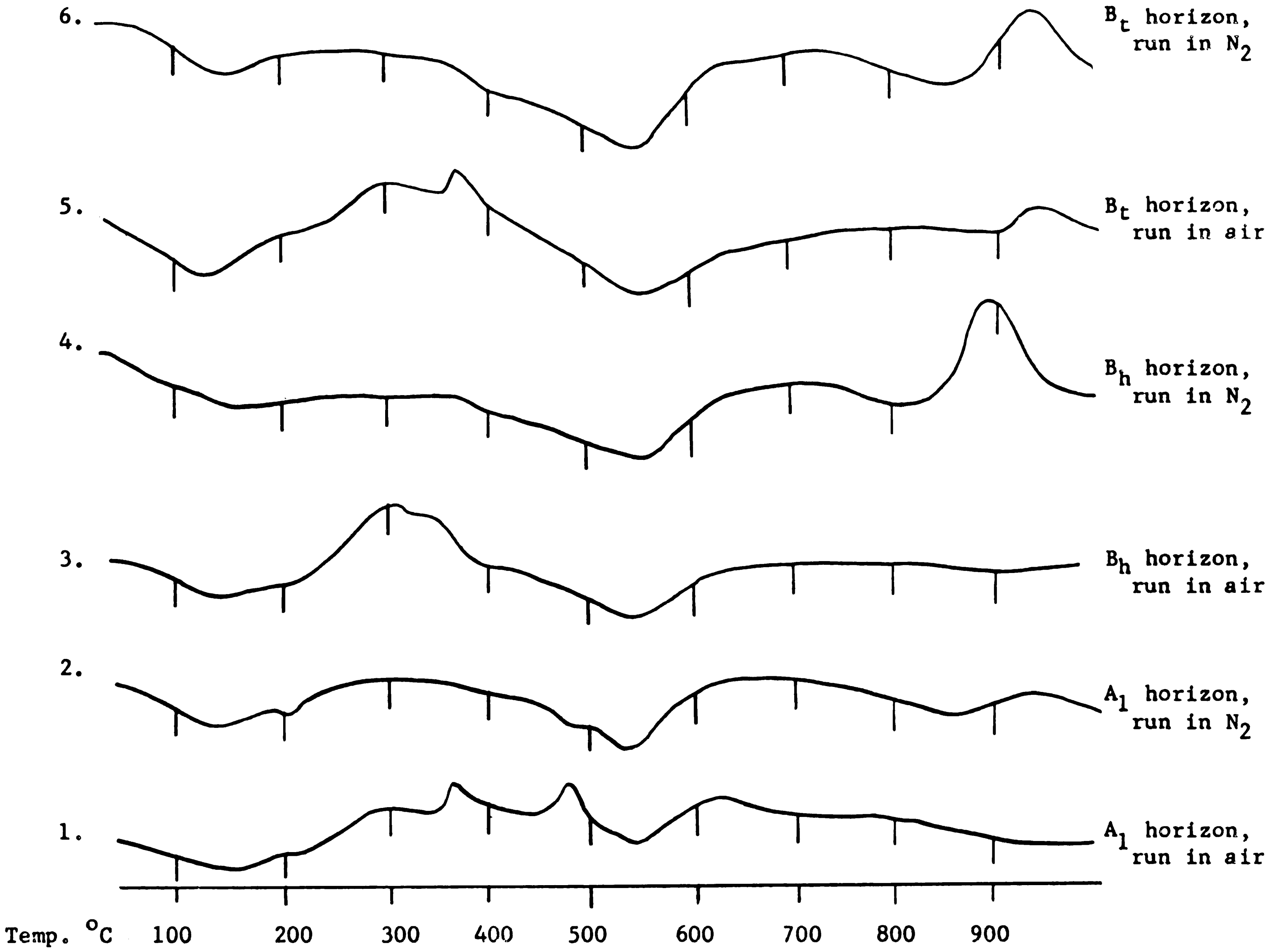

Figure 27. Differential thermal analyses curves of the less than two micron fraction of Blue Lake sand after treatment with H_2O_2.

the sample. Thus, not enough clay was present to be observed with the sensitivity used.

It is not in the scope of this thesis to investigate the interpretations of differential thermal analyses curves of soil clays when oxidation has been eliminated. Rather, based on the results of one soil profile, it is suggested that this method may be useful for future studies of soils which are high in organic matter.

CHAPTER VII

SUMMARY AND CONCLUSIONS

A theoretical discussion of the nature of heat flow within a differential thermal analysis sample holder was presented. It was shown that a simple relationship exists between the area of the differential thermal peak recorded and the heat change in the sample during a reaction if the differential thermocouple is exactly centered, the heat conductivity of the sample holder much greater than that of the sample, and there is no vertical heat flow. The theoretical discussion was in agreement with the calibration curve made using nine different salts with known heats of inversion or fusion.

A comparison was made of the heat of reactions for decomposition of magnesite and dehydroxylation of kaolinite as determined using the Clausius-Clapeyron equation and the standard curve prepared using the pure salts. The deviation was less than four per cent for both materials. The average value obtained by the two methods for decomposition of magnesite was 27.6 kilocalories per mole. This is much higher than the value of 10.1 reported in the literature but very close to the theoretical 27.8 kilocalories per mole. The average heat of dehydroxylation of kaolinite as determined by the two methods was 156 kilocalories per gram of material. It was concluded that either method was satisfactory for determination of heats of reaction and that each system must be evaluated to determine which method would be most satisfactory.

A study was made of the heats of desorption of NH_3, methylamine, and ethylamine from bentonite clay. Evidence obtained showed that the exothermic peak near 500 degrees centigrade reported by other workers is due to oxidation of NH_3 catalyzed by the platinum thermocouples. A method was developed to eliminate oxidation without using flowing gas during differential thermal analysis. The method consisted of evacuating the system and then introducing nitrogen gas, free of oxygen, into the system under slight pressure. This procedure was repeated three times and the sample allowed to pretreat for one hour with nitrogen gas passing through the sample under a slight pressure. The flow of gas was stopped and the pressure reduced to atmospheric pressure prior to making a differential thermal analysis. The following conclusions are drawn from the heats of reaction data and data concerning weight loss and nitrogen loss upon heating:

1. Below 200 degrees centigrade the entire weight loss may be attributed to water. From 200 to 400 degrees centigrade nearly equal weights of water and NH_3 are lost. Above 400 degrees centigrade increasing amounts of a weight loss which is attributed to dehydroxylation occurs.

2. The average heat of desorption of NH_3 between 200 and 450 degrees centigrade is 35.3 kilocalories per mole of NH_3 lost. Only part of this energy may be attributed to the desorption of NH_3 since water is lost at the same time.

3. The water loss between 200 and 450 degrees centigrade is not due to low temperature dehydroxylation. It is postulated that this water loss arises from decomposition of $Al(OH)_3$ to yield Al_2O_3 and water.

4. The average heat of desorption of methylamine between 200 and 450 degrees is 40.9 kilocalories per mole of methylamine lost. As in the case of NH_3, a portion of the heat absorbed must be attributed to loss of equal amounts of water. Slightly more heat appears to be absorbed by loss of methylamine than NH_3.
5. Reactions involving ethylamine are accompanied by large water losses; consequently, no value can be associated with desorption of ethylamine.

Differential thermal analyses were made of formic acid, acetic acid, methanol, and ethanol saturated bentonite. In all cases, some of the compound was held by the bentonite, but the bonding energy was not measurable.

Studies were made of the heats of desorption of NH_3, methylamine, and ethylamine from vermiculite; however, the base line drifted during differential thermal analysis indicating changes in the heat capacity and/or thermal diffusivity of the sample upon heating. Consequently, the values obtained are not expected to be valid.

It was shown that the method of eliminating oxidation with nitrogen gas during differential thermal analysis could be applied to soils high in organic matter yielding differential thermal analyses curves characteristic of the mineral components of the soils.

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