



Calhoun: The NPS Institutional Archive
DSpace Repository

Theses and Dissertations

1. Thesis and Dissertation Collection, all items

1951

The differential thermal analysis of certain clay minerals

Merritt, Harold W.; White, Ervin E.

Rensselaer Polytechnic Institute, Troy, N.Y.

<https://hdl.handle.net/10945/14068>

Downloaded from NPS Archive: Calhoun



Calhoun is the Naval Postgraduate School's public access digital repository for research materials and institutional publications created by the NPS community. Calhoun is named for Professor of Mathematics Guy K. Calhoun, NPS's first appointed -- and published -- scholarly author.

Dudley Knox Library / Naval Postgraduate School
411 Dyer Road / 1 University Circle
Monterey, California USA 93943

<http://www.nps.edu/library>

A DIFFERENTIAL THERMAL ANALYSIS OF
CERTAIN CLAY MINERALS

H. W. MERRITT, JR. AND
E. E. WHITE

THESIS
M54

Library
U. S. Naval Postgraduate School
Monterey, California

THE DIFFERENTIAL THERMAL ANALYSIS

OF

CERTAIN CLAY MINERALS

Submitted to
the Faculty of
Rensselaer Polytechnic Institute

In Partial Fulfillment of the Requirements
for the Degree of
Master of Civil Engineering

by

Harold W. Merritt, Jr. and Ervin E. White

June 1951

PREFACE

It is the purpose of this investigation to check the results of a previous study, made in 1950 by Dalton Hoskins and Richard I. Hudson, on the identification of certain clay minerals by differential thermal analysis. The check of these results is to be made by using similar techniques, procedures, clay samples and equipment.

It is the further purpose of this study to ascertain the effect of certain variable factors such as heating rate, grain size, weight of sample, ratio of sample weight to standard weight, pre-treatment, and ion saturation, which influence a quantitative differential thermal analysis of three clay minerals, viz., kaolinite, bentonite and an illite.

ACKNOWLEDGEMENTS

To Professors Edward James Kilcawley and Stanley Vincent Best for providing the background material which not only aroused interest in this study, but also made it possible, for permitting complete freedom of investigation, for encouragement in particular phases of the study, and for many suggestions which proved invaluable to the progress of the work.

To Assistant Professor John Emil Munzer for our indoctrination and patient assistance in the operation and maintenance of the testing equipment, for assistance in the assembly and calibration of additional testing equipment and for much technical advice.

To Messrs. Warren F. Savage and Sheridan S. Smith of the Metallurgical Engineering Department for their assistance and advice in the preparation and calibration of numerous thermocouples and for timely help in the testing of our electronic recording equipment.

CONFIDENTIAL

The following information was obtained from a review of the records of the [redacted] and is being furnished to you for your information. It is requested that you keep this information confidential and not disseminate it to any other personnel. The information is being furnished to you for your information and is not to be used for any other purpose. If you have any questions, please contact the [redacted] at [redacted].

The information is being furnished to you for your information and is not to be used for any other purpose. If you have any questions, please contact the [redacted] at [redacted].

CONTENTS

| | |
|---------------------------------------|----|
| HISTORY | .1 |
| THEORY. | .4 |
| EQUIPMENT | 11 |
| EQUIPMENT CALIBRATION | 15 |
| PROCEDURE | 17 |
| RESULTS AND CONCLUSIONS | 24 |
| COMMENTS AND RECOMMENDATIONS. | 45 |
| REFERENCES | |
| APPENDIXES | |

CONTENTS

i. Introduction 1

ii. The History of the 10

iii. The Development of the 20

iv. The Present Position of the 30

v. The Future of the 40

vi. The Conclusion 50

vii. Appendix 60

viii. Bibliography 70

ix. Index 80

HISTORY

Le Chatelier (1887) is credited with suggesting the method of differential thermal analysis and with conducting the initial investigations using this method. In 1904 Saladin and Le Chatelier presented a paper describing a modified apparatus but were unable to obtain strictly reproducible curves.

Improved technique and apparatus developed an interest in the application of the method to a study of clays and soils. Wallach (1913) studied clays and Wohlon (1913) examined clays, bauxite, and allied materials. Differential thermal analysis was applied to similar substances by Houldsworth and Cobb (1922) and Kurnakov and Urazov (1924).

It hasn't been until recent years that recording and temperature control equipment have been available with which investigators could obtain reproducible curves or semi-quantitative information. The present-day intensified study of the method began in France with Orceel and Caillere (1933) and in the United States with Insley and Ewell (1935).

During this period, many papers on differential thermal analysis were presented, notably:

Caillere (1933-1934), Dubois (1936),

Kazakov and Andrianov (1936) on methods used in differential thermal analysis.

Kumanin and Kalen (1936) on theory.

Menshutkin (1936) on history.

Orcel (1935) on laterites.

Thilo and Schunemann (1937) on pyrophyllite

Wilcox and Bossard (1936) on self-recording apparatus.

Norton (1939) on an evaluation of the method as applied to clay minerals.

Orcel in 1935 presented a paper giving thermal curves for most of the clay minerals and many natural clays. Although Orcel suggested a possibility of quantitative measurement, no such analysis was attempted until 1938 when Norton presented his paper.

The most recent applications of differential thermal analysis have been numerous and varied.

Of primary interest to the soils engineer are the critical studies of many clay minerals by Grin and Rowland (1942) and basic information on the general application of the method presented in papers by Speil, Berkelhamer, Pask and Davis (1945).

Kerr and Kulp (1947, 1948, and 1949) have considerably added to the available information in their application of a semi-quantitative method of differential thermal analysis to a study of clay mineral regions throughout the United States for the American Petroleum Institute. These investigators have also introduced a multiple method of differential thermal analysis whereby it has been possible to complete 18 tests in a normal eight-hour working day. (1)

Work on the identification of clay minerals by differential thermal analysis was initiated at Rensselaer Polytechnic Institute in 1948 by Costello, who used a tube furnace for heating the samples, measured the temperatures and differential temperatures with a portable potentiometer, and controlled the heating rate by manually operating the Varic. The following year Bystrowski added a Speedomax for recording the sample and differential temperatures but continued to manually control the heating rate. During the summer of 1949, Mr. J. E. Munzer added a Brown Potentiometer - to record the standard temperature and to automatically control the heating rate - and assembled the equipment in the form used by Hudson and Hoskins for their work in 1950.

THEORY

Differential Thermal Analysis

The theory of differential thermal analysis was outlined by Speil in 1945. This theory was later modified by Kerr and Kulp in 1948 (1) and is included in this study as an aid to interpreting the test results which follow.

Two methods are used in the study of the thermal properties of minerals. One method, equilibrium dehydration, uses a static method of heating and is concerned with the determination of the percent loss in weight as a function of temperature. Because of the inherent difficulties in this method of analysis, it is generally believed that differential thermal analysis offers greater possibilities for the study of clay mineral structure.

Differential thermal analysis consists of comparing the thermal properties of an active substance with those of a thermally inactive material, such as alumina, by heating the materials at a constant rate up to a temperature of approximately 1100° C.

The temperatures of both the active and inert materials are measured by separate thermocouples, and the difference in temperature between the two materials is measured by a differential thermocouple

bridging the two substances. Suitable equipment records the temperatures at which the thermal changes take place as well as the intensities of these reactions. The final results appear as a curve showing the temperature difference between the active and inert materials--usually expressed in millivolt equivalents--as a function of the temperature of the active material.

The thermal changes which take place in the active materials are dehydration and decomposition. Dehydration produces an endothermic reaction during which the sample absorbs more heat than the standard causing the temperature of the sample to lag behind that of the standard. This temperature lag introduces an electrical potential in the differential thermocouple which causes a displacement of the differential temperature curve in a negative direction.

Decomposition produces an exothermic reaction resulting from a break-down of the original crystalline structure during which heat is liberated from the active material causing the temperature of the sample to be higher than that of the standard. The direction of the electromotive force in the differential thermocouple due to an exothermic reaction is opposite to that of the flow caused by an endothermic reaction and

results in a displacement of the differential temperature curve in a positive direction.

If the sample and standard material are at the same temperature, no electromotive force occurs and the differential thermal curve registers zero millivolts.

Since the space does not permit a complete derivation of the differential thermal analysis equations, the reader is referred to the paper by Kerr and Kulp (1) in which this derivation is presented.

The equation developed by Kerr and Kulp considers the dynamic effects of the differential flow of heat from the sample block to the thermocouples in the center of the sample and the heat of the thermal reaction. This equation was obtained by equating the following three items:

1. The quantity of heat added or subtracted from the test specimen due to exothermic or endothermic reactions.
2. The quantity of heat brought in by flow from the metal block and absorbed by the specimen and standard.

3. The amount of heat used in raising the temperature of both the active and inert material.

Thus:

$$m = \frac{gk}{\Delta H} \int_a^c \frac{\Delta T}{dt}$$

Where: m = the mass of reactive material in the specimen

g = geometrical shape constant

k = thermal conductivity of the test specimen

ΔH = heat of reaction per unit mass of the reacting material.

ΔT = the temperature difference indicated by the differential thermocouple

dt = a differential interval of time

a and c = the integral limits of the differential temperature curve for an endothermic or exothermic reaction.

The derivation of the above equation neglects the temperature gradient in the system by assuming that it is essentially the same for both the active and inert materials. Furthermore, the derivation assumes that the mass of both the test specimen and standard are equal and that temperature differences between the nickel block and standard material as well as differences due

THE UNIVERSITY OF CHICAGO

CHICAGO, ILL.

$$\frac{d}{dx} \int_a^x f(x) dx = f(x)$$

THE UNIVERSITY OF CHICAGO

CHICAGO, ILL.

THE UNIVERSITY OF CHICAGO

CHICAGO, ILL.

CHICAGO, ILL.

THE UNIVERSITY OF CHICAGO

CHICAGO, ILL.

THE UNIVERSITY OF CHICAGO

CHICAGO, ILL.

CHICAGO, ILL.

THE UNIVERSITY OF CHICAGO

CHICAGO, ILL.

CHICAGO, ILL.

THE UNIVERSITY OF CHICAGO

CHICAGO, ILL.

THE UNIVERSITY OF CHICAGO

CHICAGO, ILL.

CHICAGO, ILL.

CHICAGO, ILL.

CHICAGO, ILL.

THE UNIVERSITY OF CHICAGO

CHICAGO, ILL.

to changes in the mean specific heat and thermal conductivity of the test specimen are small compared to those produced by other factors.

The above equation demonstrates that the area under the differential temperature curve is proportional to the mass of the reacting material. Since the geometrical shape factor and the heat of reaction are constant for a given material and test conditions, the above relation would be lineal if the thermal conductivity of the materials remained constant throughout the test. It has not been demonstrated that the thermal conductivity remains constant.

Selecting the limits of the differential temperature curve is purely arbitrary, and the area under the curve must be laboriously computed. Hence, most investigators concerned with a quantitative analysis are content with establishing the relation between the amplitude of the peak reaction and the quantity of the active material contributing to the reaction. It is this method which will be used in the investigation that follows.

Clay Mineral Structure

The general thermal characteristics of the three clay minerals investigated are discussed as follows:

Kaolinite: The thermal curve exhibits an endothermic reaction at about 600° C and an abrupt intense exothermic reaction near 1000° C. Most investigators agree that the endothermic reaction accompanies the dehydration of the mineral and the exothermic reaction is associated with the formation of gamma-aluminum oxide.

Illites: The thermal curves show endothermic peaks at about 150° C., 600-650° C., and about 950° c., and an exothermic peak immediately following the third endothermic peak. The first endothermic peak indicates the loss of swelling water (water held between the basal planes of the lattice structure), the second endothermic peak accompanies the loss of most of the lattice water, and the third endothermic peak is associated with the final destruction of the illite structures. The exothermic peak is probably associated with the formation of spinel.

Bentonite: The thermal curves show endothermic peaks at about 150° C., 775° C., and an exothermic peak immediately following the last endothermic peak. The initial endothermic peak, as in the curves for illites, represents the loss of swelling water, the second

endothermic peak accompanies a loss of lattice water. The reason for the third endothermic peak is not fully agreed upon by all investigators. Grim and Rowland (2) suggest that it is associated with lattice disruption, whereas Page (3) maintains that it is due solely to the loss of the remaining lattice water. The exothermic peak probably accompanies the formation of spinel.

The kaolinite and illites both have an endothermic reaction between 500 and 600° C. However, the intensity of the kaolinite reaction is about ten times that of the illite. This can be partially explained by the fact that the 1:1 lattice clay mineral (kaolinite) loses more water than the 2:1 lattice clay mineral (illite); furthermore, Grim and Rowland suggest that this reaction also represents the destruction of the 1:1 lattice. The kaolinite curves are more regular and show less variation than the illite curves. It has not been satisfactorily explained why the second endothermic peak occurs at about 100° C higher in bentonites than in illites, when both clay minerals have the 2:1 lattice and about the same amount of lattice water. The third endothermic peak appears to be characteristic of 2:1 lattice clay minerals.

EQUIPMENT

General Description

The equipment used throughout the study was the same as that used by Hudson and Hoskins in 1950 except for the addition of two furnaces to increase the number of tests which could be conducted and to more fully utilize the relatively expensive autographic recording equipment.

Sample Holders

The sample holders--developed by J. E. Munzer--were machined from a nickel block. Each holder has two cells, one for the test sample and the other for the standard, separated by a slot $1/16$ inch wide and $\frac{1}{2}$ inch deep to reduce heat transfer between the cells. Each cell contains a temperature--measuring thermocouple and a differential-temperature thermocouple which connects the two cells. The sample holder was mounted on a rod about 14 inches long to facilitate placing and removing the holder from the furnace. Stainless steel rods were found to be the most effective in resisting oxidation at the high furnace temperatures.

Thermocouples

All thermocouples were made from Brown and Sharp 18 gage chromel and alumel wire stock and were fused with a fine-tipped oxy-acetylene torch using borax

MEMORANDUM

The following information was obtained from the records of the Department of the Interior, Bureau of Land Management, on the subject of the land owned by the United States in the State of California, and is hereby published for the information of the public.

The total area of land owned by the United States in the State of California is approximately 100,000,000 acres.

LAND OWNERSHIP

The land owned by the United States in the State of California is divided into several classes, as follows:

1. Public Domain Land: This class includes all land owned by the United States which has not been surveyed, patented, or otherwise disposed of.

2. Surveyed Land: This class includes all land which has been surveyed but not patented or otherwise disposed of.

3. Patented Land: This class includes all land which has been patented to private individuals or corporations.

4. Land Reserved for Public Use: This class includes all land which is reserved for public use, such as national parks, forests, and monuments.

5. Land Reserved for Indian Use: This class includes all land which is reserved for the use of Indian tribes.

6. Land Reserved for Military Use: This class includes all land which is reserved for military use, such as forts and arsenals.

7. Land Reserved for Naval Use: This class includes all land which is reserved for naval use, such as harbors and shipyards.

8. Land Reserved for Agricultural Use: This class includes all land which is reserved for agricultural use, such as irrigation canals and water rights.

CONCLUSION

The above information is based on the best available records and is subject to change as more information becomes available.

as a flux. The differential thermocouple consists of two leads of chromel wire bridged by a short length of alumel wire. The thermocouple junctions were centered in the cells and were held in place by porcelain tube insulators which also carried the thermocouple leads to the exterior of the furnace. Connection of the thermocouples to the automatic recording equipment was made through a Jones plug mounted on the table supporting the furnaces. Additional leads connected the Jones plug to a terminal block in the recording equipment cabinet. Such a connection facilitated the operation of the three furnaces with one set of recording equipment, but in order to make the necessary corrections, the temperature at each cold junction must be noted.

Furnaces

The three test furnaces used were heavy duty, combustion type, Hoskins Model FH-305, 12 inches long with an inside diameter of 2-1/32 inches and were lined with an alumina tube having an inside diameter of 1-1/2 inches. It was the original intent to use 1750-watt heating elements supplied by a two-kilowatt transformer with a maximum output of 17 volts and 118 amperes. However, certain operation difficulties, discussed in Appendix H, made it necessary to revert two of the furnaces to 1000-watt elements

supplied by a one-kilowatt transformer having a secondary output of 20 volts and 50 amperes.

Temperature Control

The rate at which the temperature control indicator (black pointer) travels across the Brown Potentiometer is established by the ratio of gears in the chain-drive mechanism. The furnace temperature indicator (red pointer) registers the temperature of the standard in the sample holder. The relative position of this indicator with respect to the temperature control indicator adjusts (by means of a cam and lever device) the position of a motor-driven variable transformer, Variac V-20, having a rated output of 3.45 kilowatts and operating between 0 and 135 volts. The Variac controls the voltage to the primary of the furnace transformer and thereby maintains the desired rate of temperature increase.

Recording Equipment

A Brown Recording Potentiometer Pyrometer, Model No. 113661-X53#1H, manufactured by the Brown Instrument Company, having a temperature range of 0 to 1200 degrees centigrade, was used to continuously record the temperature of the standard and to control the rate of increase in furnace temperature as described above.

The sample temperature and differential temperatures were recorded by a Typo G, Model S 60000 Series, Speedonax, manufactured by Leeds and Northrup Company. The Speedonax has a temperature range of 0 to 1200 degrees centigrade and can record differential temperatures from plus to minus 1.5 millivolt equivalents. This multiple-point recording apparatus, when operated as a two-point recorder, plots thermal curves directly, successive points on each curve being printed every six seconds. Since the thermal curves are printed on paper calibrated in degrees centigrade, the temperature of the sample can be read directly from the record sheet, but the evaluation of the differential thermal curve requires the superposition of an equivalent millivolt scale.

Preparation Apparatus

Materials to be tested were preheated in an Elconap Oven, Model DPC-M-60292. Thermocouple calibrations were made in a Hevi-Duty Multiple Unit Electric Muffle Furnace, Type 66-P, with a maximum temperature of 1000 degrees centigrade. A Conco-Moinzer Sieve Shaker, Cat. No. 18480, was used for sample fractionation. Dispersed samples of the illite were centrifuged in an International Centrifuge, Size 1, Type C, No. X8982, manufactured by the International Equipment Company.

EQUIPMENT CALIBRATION

Thermocouples

The calibration of the thermocouples was necessary to prevent the use of faulty thermocouples and to permit a more exact analysis of the data obtained from each test. By calibrating each thermocouple against a standard thermocouple, corrections can be made for slight variations.

All thermocouples were calibrated by placing them in the Muffle Furnace with a standard thermocouple and heating them to a temperature of 1000 degrees centigrade. The standard thermocouple had been previously calibrated by Hudson and Hoskins. To obtain consistent results, the cold junction temperatures and the e.m.f. of both the test and standard thermocouples--measured by a Brown Portable Potentiometer--were recorded as the furnace cooled. By using two portable potentiometers, it was possible to calibrate four thermocouples at one time. Each thermocouple was numbered so that it could be identified in the assembly of the sample holders and properly identified with the data for each test conducted.

Differential Thermocouples

The differential thermocouples were calibrated to eliminate those which were faulty and to establish

the zero base line of the differential thermal curve for the particular differential thermocouple. A differential thermal test on an assembled sample holder, using an equal quantity of alumina in both the sample and standard cell was sufficient to both check and calibrate the differential thermocouple.

Recording Equipment

The recording equipment was adequately calibrated during its initial installation by J. E. Munzer and by Hudson and Hoskins. Only occasional checks with a portable potentiometer were found necessary.

PROCEDURE

Samples and Standard

Samples of the three clay types tested were kaolinite from Georgia (Wards' Natural Science Establishment, Inc.); Volclay Wyoming bentonite (American Colloid Co.); and grundite bond clay, an illite-bearing shale from Goose Lake, Illinois.

The clay samples were ground and sieved to give variations in grain size from 100 to 140 mesh, 140 to 200 mesh, and from 200 to pan. Samples having a grain size from 140 to 200 mesh were used on all studies except those concerned with the effect of grain size variation on the differential thermal curve. The sieved material was placed in evaporating dishes in a drying oven set at 50° C where it remained for at least 24 hours prior to testing. Because some of the material aggregates upon drying (particularly the kaolinite) each sample was resieved immediately before being placed in the sample block.

The standard material used was electrically fused crystalline alumina (Norton Company) and was ground and sieved to give the same grain size distribution as the sample but was not oven dried. For each test, the grain size of the alumina was always the same as the grain size of the sample.

THE HISTORY OF THE

The first part of the book is devoted to a general history of the world from the beginning of time to the present day. It is written in a simple and straightforward style, and is intended for the use of students in schools and colleges. The author has endeavored to present a clear and concise account of the events of the past, and to show the progress of civilization from its earliest beginnings to the present day. The book is divided into three parts: the first part deals with the history of the world from the beginning of time to the present day; the second part deals with the history of the United States from its independence to the present day; and the third part deals with the history of the world from the present day to the future. The book is written in a simple and straightforward style, and is intended for the use of students in schools and colleges. The author has endeavored to present a clear and concise account of the events of the past, and to show the progress of civilization from its earliest beginnings to the present day.

Henceforth, the clay tested will be referred to as the sample and the alumina will be referred to as the standard.

Prior to placing the sample and standard in their individual cells, the thermocouples were checked to insure that they were not in direct contact with the sample block and that each was centered in its cell. Each insulator around the thermocouple wire was adjusted so that its cell face was flush with the wall of the cell.

The two types of tests conducted required two different procedures in preparing and placing the materials in the sample holder. Tests to check the results of the study made by Hudson and Hoskins required cell volumes of material compacted in the same manner adopted by them. The second phase of this investigation necessitated the use of known weights of sample and standard. Various weight ratios were used in order to study their effect on the magnitudes of reactions on the differential thermal curves.

Where tests required a cell volume of material, the sample and standard were placed in their respective cells and compacted by tapping the bottom of the sample block until the material was flush with the top of the cell. This was the method adopted by

Hudson and Hoskins and was used during the first phase of this investigation to permit comparison of results by insuring maximum consolidation and uniform density.

For tests requiring known weights of sample and standard, the material was received upon removal from the drying oven and was accurately weighed to within ± 0.001 gram on an analytical balance before being placed in the sample holder. The weighed material was also consolidated by tapping the bottom of the sample block.

It should be noted that in order to obtain consistent results, the thermocouples should be sufficiently covered by the material in each cell, thereby establishing a minimum amount of material which can be accurately tested.

The effect of pre-treatment on the illite-bearing shale was studied on samples of grundite prepared as follows:

As Received: The material was sieved just as it came from the containers and was tested without being oven dried.

Oven Dried: The material was sieved, placed in the drying oven at 50° C for at least 24 hours prior to being resieved and tested.

Dispersed: The grundite was dispersed in distilled water, settled, decanted, and centrifuged.

After drying at 50° C, the sample was ground and sieved before being tested.

Treated with H_2O_2 : The sample was dispersed in distilled water, treated with 30% hydrogen peroxide, settled, decanted, centrifuged, redispersed in distilled water and recentrifuged three times before being dried, ground, sieved, and tested.

Treated with H_2O_2 and HCl: A portion of the sample treated with just hydrogen peroxide was also treated with dilute hydrochloric acid prior to settling. After settling, the material was decanted, centrifuged three times before being dried, ground, sieved and tested.

Samples used in the investigation of the effects of ion saturation on the differential thermal curves were prepared by W. D. Ennis and J. C. Hufft for a thesis entitled: "Investigation of the Effect of Various Cations on the Atterberg Limits of Kaolinite, Illite, and Montmorillonite". The reader is referred to the above mentioned thesis for a description of the procedure employed in the preparation of these samples.

Operation of Equipment

After the sample and standard had been placed in the sample holder, the thermocouples were connected

to the recording equipment through the Jones plug. The batteries for operating the internal circuits of the Brown Potentiometer and the Speedomax were then connected, and the compensating rheostat was set to provide a predetermined initial voltage setting on the Variac. At this point, the switches to the furnaces and the main power supply were closed. The electronic circuit of the Speedomax is automatically balanced, but the circuit in the Brown Potentiometer must be balanced manually.

During these experiments, it has been determined that a more uniform heating rate and consequently more consistent results could be obtained by turning off the Brown Potentiometer after balancing the internal circuit and setting both indicators at 75° C. By properly setting the compensating rheostat to establish the correct initial voltage from the Variac to the furnace, and by setting the temperature control mechanism on the Brown into operation when the oven has reached a temperature of 75° C (as indicated by the Speedomax), the hunting effect of the temperature control mechanism can be virtually eliminated.

On the basis of a recommendation by Hudson and Hoskins, a heating rate of 1023° C per hour was used throughout this investigation. The heating rate is established by the ratio of gears in the chain drive

for the temperature control mechanism of the Brown Potentiometer. At a temperature of 1200° C, the temperature control indicator opens a mechanical cut-off switch which operates a relay. The activation of the relay automatically shuts off all power to the equipment and furnaces at the end of each test run.

Data Recorded:

The following data is considered to be essential for each test conducted:

1. Number of Run: To identify the Brown and Speedomax recordings with the data.
2. Date of test:
3. Sample tested: Identify by mineral name or origin.
4. Standard Used: Usually Alumina Silicato.
5. Grain size of Sample and Standard:
6. Quantity of Sample and Standard Used: By either cell volume or weight in grams. If a mixture was used, the weights of each material in the mixture.
7. Thermocouple Numbers: To correct for variation in original calibration.
8. Cold Junction Temperatures: To make the necessary corrections for cold junction variations.

THE UNIVERSITY OF CHICAGO
DEPARTMENT OF CHEMISTRY
530 SOUTH EAST ASIAN AVENUE
CHICAGO, ILLINOIS 60607
TEL: 773-936-3700

MEMORANDUM

TO: THE CHAIRMAN, DEPARTMENT OF CHEMISTRY
FROM: [Name]

SUBJECT: [Subject]

[Text]

[Text]

[Text]

[Text]

[Text]

9. Heating Rate: Both that established by the gear ratio in the Brown and that indicated on the Brown Recording.
10. Furnace Wattage: This investigation used both 1000 and 1750-watt furnaces. The results obtained from each furnace varied slightly and this variation must be corrected for in the results and should be properly accounted for.
11. Remarks: Deviations from standard procedure, equipment, material, or any other pertinent information.

1. The first part of the report is devoted to a description of the general situation in the country at the present time. It is found that the country is in a state of general depression, and that the people are suffering from want and distress. The cause of this is attributed to the war, and the consequent destruction of property and the loss of life.

2. The second part of the report is devoted to a description of the state of the different branches of industry and commerce. It is found that the different branches of industry and commerce are all in a state of depression, and that the people are suffering from want and distress. The cause of this is attributed to the war, and the consequent destruction of property and the loss of life.

3. The third part of the report is devoted to a description of the state of the different branches of agriculture. It is found that the different branches of agriculture are all in a state of depression, and that the people are suffering from want and distress. The cause of this is attributed to the war, and the consequent destruction of property and the loss of life.

4. The fourth part of the report is devoted to a description of the state of the different branches of education. It is found that the different branches of education are all in a state of depression, and that the people are suffering from want and distress. The cause of this is attributed to the war, and the consequent destruction of property and the loss of life.

RESULTS AND CONCLUSIONS

General

During the process of evaluating the 200 or more tests conducted during this investigation, certain fundamental properties of the differential temperature curve became apparent. These properties are discussed at this point to assist in the explanation of the results and conclusions which follow.

As has been noted by other investigators, the temperatures at which the peak endothermic and exothermic reactions took place are a particular property of each clay mineral. It is this property which makes possible the identification of clay minerals by differential thermal analysis.

The theoretical discussion indicated that the areas under the differential temperature curves (and hence the magnitudes of the peak reactions) are proportional to the mass of the reacting material. This fact makes possible quantitative analysis of clay minerals by differential thermal analysis.

Certain tests, notably those on the effect of variations in grain size (Appendix C), evidenced a constant displacement of the differential temperature curve with respect to the zero

...the ... of ...
 ...the ... of ...
 ...the ... of ...
 ...the ... of ...
 ...the ... of ...

...the ... of ...
 ...the ... of ...
 ...the ... of ...
 ...the ... of ...
 ...the ... of ...

...the ... of ...
 ...the ... of ...
 ...the ... of ...
 ...the ... of ...
 ...the ... of ...

...the ... of ...
 ...the ... of ...
 ...the ... of ...
 ...the ... of ...
 ...the ... of ...

millivolt line of the Speedomax. Other tests, using known weights of the sample and varying weights of standard, revealed that the magnitudes of the reactions for equal weights of the sample remained constant when measured from the displaced base line of the curve and that the magnitudes were not apparently effected by the displacement. The displaced base line was taken to be those portions of the differential temperature curve which were known to exhibit no thermal reactions.

From these tests the authors concluded that two factors must be responsible for the displacement of the differential temperature curve. These factors are the relative thermal conductivities of the sample and standard and the relative mean specific heats of the sample and standard. Of these two factors, the relative thermal conductivity is considered to be more influential on the observed displacement. Furthermore, it is this factor which is considerably affected by the relative physical position of the thermocouples in the sample and standard cells and the method used in placing and compacting the materials in the cells.

The influence of the relative thermal conductivity on the displacement of the differential temperature curve can be analyzed by a study

of the equation for a steady state of heat flow.

$$q = KA \frac{T_0 - T_1}{d}$$

Where q = the time rate of heat flow

K = the thermal conductivity

A = the area measured perpendicular to the direction of heat flow

T_0 = the temperature of the nickel block

T_1 = the temperature at the center of the cell

d = the distance measured in the direction of heat flow

Let $\frac{A}{d} = g$, the geometric shape factor (see THEORY), which is the same for both cells. Since the rate of heat flow (q) is the same from the block to sample and standard, the difference in temperatures between the nickel block and center of the cell ($T_0 - T_1$) is inversely proportional to the conductivity (K). Thus, if the conductivity of the sample material were lower than that of the standard, the temperature difference, $T_0 - T_1$, would be consistently greater for the sample than for the standard. Hence, the temperature recorded by the thermocouple in the sample would be constantly lower than that recorded by the thermocouple in the standard, provided of course, that no heat was being absorbed or liberated by the sample itself. From the description of the

operation of the differential thermocouple contained in the section on THEORY, it can be seen that this difference in temperature between the sample and standard would cause a constant displacement of the differential temperature curve in an endothermic direction. A displacement in the opposite direction would result if the thermal conductivity of the standard were lower than that of the sample.

From the foregoing, three important conclusions have been reached:

1. The zero base line of the differential temperature curve is a relative function of the materials being tested and is not necessarily a characteristic of the equipment used in conducting the tests.
2. The magnitudes of the thermal reactions, measured from the displaced zero base line of the differential temperature curve, are not affected by the displacement.
3. The evaluation of a differential temperature curve and particularly a quantitative differential thermal analysis should be made with respect to the displaced zero base line of the curve.

The location of the displaced base line is a factor which has presented a great deal of

difficulty in previous attempts of a quantitative differential thermal analysis. A change in the relative thermal conductivities or mean specific heats during a test can cause a change in the position of this reference line. Most important, a slight variation in the location of the base line can cause a slight change in the amplitude of the peak reactions and a considerable change in the area under the differential temperature curve, thus giving an erroneous indication of the mass of active material in the sample.

Verification of Previous Results

The portion of this investigation concerned with the verification of previous results is evaluated in the following sections.

Heating Rate:

Hudson and Hoskins concluded from their study of the effect of various heating rates on the differential thermal curve that a lower heating rate results in a smaller amplitude of reaction. These results were accepted without verification because they are in agreement with theory. A low heating rate increases the period of time over which a given temperature change takes place. The area under a differential temperature curve represents the energy liberated or absorbed by the active material for a certain change in temperature and is independent of the heating rate.

Therefore, for a low heating rate the reaction would extend over a large period of time and the amplitudes of the reactions would be small. Conversely, for a high heating rate the reaction would extend over a short period of time. For the same liberation or absorption of energy, the area under the thermal curve would also be the same. Thus, the amplitudes of the reactions for a high heating rate would be larger than those of a low heating rate.

The use of a low heating rate would give greater sensitivity in the control and recording of thermal reaction temperatures but would necessitate the use of suitable equipment to amplify the differential temperatures. The heating rate of 1023° C per hour used throughout this investigation is considered to be an optimum for the particular equipment employed without amplifiers.

Grain Size of Thermal Standard:

Hudson and Hoskins conducted a series of tests in which alumina was used as both the sample and standard material. The grain size of the standard remained constant at 60 - 100 mesh while the grain size of the sample was decreased from 60 - 100 mesh to 200 - pan. A review of the data obtained from these tests revealed a constant

displacement of the differential temperature curve in an endothermic direction. This displacement increased as the grain size of the sample decreased.

The above effect can be explained by the fact that the thermal conductivity of a granular material decreases as the grain size of the material decreases. The conductivity decreases because the total number of voids increases while the size of the voids becomes smaller for a given volume of material compacted to the same density. From the foregoing general discussion it can be seen that the reduced conductivity of the smaller grain sizes should cause a displacement of the thermal curve in an endothermic direction.

Hudson and Hoskins conducted further tests using a constant grain size of 60 - 100 mesh for the alumina standard but varying the grain size of a kaolinite sample. Once again a displacement of the thermal curve could be detected. This displacement increased in the endothermic direction as the grain size of the kaolinite decreased, which is again consistent with the above observation. It is therefore concluded that the relative grain sizes of thermal standard and sample affects the location of the differential temperature curve with respect to the zero millivolt

line of the Speedomax. It is believed that Hudson and Hoskins were essentially correct in using the same grain size for both sample and standard in an endeavor to eliminate this effect.

Grain Size of Clay Mineral:

The following two observations were made as a result of the studies on the effect of varying the grain size of the clay mineral:

1. There is a variation in the magnitudes of peak reactions with different grain sizes.
2. There is a displacement of the thermal curve which changes with varying grain sizes.

It has been demonstrated theoretically that the area under the differential temperature curve (and hence the amplitude of the peak reaction) is proportional to the mass of the reacting substance. Actual weight measurements were made by Hudson and Hoskins to confirm the fact that the amount of material tested in a given cell volume decreased with decreasing grain size. It should therefore be expected that the magnitudes of both the exothermic and endothermic reactions should decrease with decreasing grain sizes of all three clay minerals tested. Grain size studies made during this investigation confirmed the above expectations. (See Appendix C).

Hudson and Hoskins concluded from their studies of variation in the grain size of clay

minerals that the intensity of the endothermic reaction of kaolinite decreased with decreasing grain size, whereas the intensity of the second and third endothermic reactions of bentonite and illite increased with decreasing grain size.

Hudson and Hoskins also observed that the thermal curves for kaolinite were increasingly displaced in an exothermic direction while the displacement of the bentonite and illite curves increased in an endothermic direction. Since the curves were drawn with respect to the zero millivolt line of the Spoodomax, this displacement was sufficient to indicate that the reactions increased with decreasing grain size. However, by measuring the magnitudes of the reactions from the displaced base line (taken as the tangent to the position of the curve between the second and third endothermic reactions) no variation in the intensities of the reactions for bentonite and illite could be detected.

The magnitudes of the peak reactions of bentonite and illite are considerably smaller than those of kaolinite. Hence, a small difference in the amount of material tested, the manner in which it is compacted, a slight variation in heating rate, the length of time which the material is left in the drying oven, or even a

slight variation in the sample itself would be sufficient to nullify a difference in the amplitude of the reactions.

The curves showing the effect of variation in grain size in Appendix C were also plotted with respect to the zero millivolt line of the Speedo-max. The displacement of the curves for all three clays increases in an exothermic direction. Only a difference in technique could account for the deviation in this direction of displacement of the bentonite and illite curves prepared by Hudson and Hoskins.

Since the thermal conductivity of both the sample and standard decreases with decreasing grain size, the increased displacement of the curves in the exothermic direction obtained by this investigation can be explained only if the rate of decrease in conductivity of the standard is greater than that of the sample. It is logical to assume that the rate of change in the size and number of voids between the flat, plate-shaped, clay-mineral particles is slower than that of the more spherical alumina crystals.

Standard Differential Thermal Curves:

Verification of standard differential thermal curves for illite was not possible because a

different illite-bearing material was used throughout this investigation. Though the curves exhibit small endothermic reactions at about 600°C and 900°C which are typical of illite, they also show a large exothermic reaction near 500°C which is not reported by other investigators. Thus it can be concluded that the illite-bearing shale (grundite) contains but a small portion of illite clay.

By using essentially the same techniques adopted by Hudson and Hoskins it was possible to duplicate the differential thermal curves of kaolinite and bentonite with sufficient accuracy for a qualitative analysis. However, the duplication was not considered sufficiently accurate for a quantitative analysis. The magnitudes of the peak reactions obtained were consistently lower than those obtained by Hudson and Hoskins, indicating that the amount of material placed in a given cell volume was consistently less throughout this investigation. It is therefore concluded that though one operator can achieve consistent results using a given cell volume of material, duplication of results sufficiently accurate for a quantitative analysis requires the use of known weights of the active material being tested.

Factors Affecting A Quantitative Analysis

Two methods of effecting a quantitative

differential thermal analysis have been proposed. One method consists of comparing the magnitudes of the peak reactions of the unknown sample with the corresponding magnitudes of peak reactions for the same volume or weight of a pure mineral sample. A second method consists of preparing a calibration curve showing the variation in magnitude of peak reactions as a function of the percent of pure mineral present in a controlled mixture of mineral and inert substance. The magnitudes of the peak reactions of a thermal curve for an unknown sample are then used to determine from the calibration curve the percent of a given mineral present in the sample. Since the results of both methods are dependent upon a comparison, it is essential that certain factors which influence the thermal reactions be properly evaluated and controlled. A discussion of these factors follows.

Heating Rate and Grain Size:

The effect of variations in heating rate and grain sizes of materials tested has been previously discussed. Thus, to obtain comparable results the heating rate used should be the same for all tests. In addition, the grain size of the unknown sample tested should be the same as that of the materials used in developing either standard differential

temperature curves or weight-calibration curves.

Pretreatment:

Since the grundite bond clay was known to contain but a small portion of illite, it was deemed necessary to treat the material in various manners in an effort to obtain measurable differential temperature reactions. The curves obtained are presented in Appendix D and show conclusively that the method of preparing a sample for differential thermal analysis affects the shape of the differential temperature curve. Since the curves were plotted with respect to the zero millivolt line of the Speedomax they also exhibit notable differences in displacement.

The thermal curve of the material tested without previous treatment indicates - by the endothermic displacement of the curve - either a low thermal conductivity or low mean specific heat or both. This curve also has a large initial endothermic reaction indicating the presence of a considerable amount of absorbed basal plane moisture (swelling water).

The thermal curve obtained after drying the sample 24 hours at 50° C indicates that most of the swelling water was removed and that the thermal conductivity or heat capacity of the material was increased.

Dispersing the material in distilled water increased the amplitude of the reactions.

Treating the dispersed sample with H_2O_2 did not appreciably affect the differential temperature curve, thereby indicating that little organic matter was present in the original material.

The thermal curve of the sample treated with hydrochloric acid evidences a change in structure of the original material by a shift in the temperature at which the initial exothermic reaction occurred. This would suggest that an excess of hydrochloric acid has been used in the treatment. It is also interesting to note that this curve exhibits larger endothermic reactions which undoubtedly are due to the increased presence of hydroxyl ions in the crystal lattice structure.

Clay samples prepared by Ennis and Hufft for their work on ionic exchange (4) were made available for differential thermal analysis, and curves resulting from this study are also presented in Appendix D. These curves present further evidence that preparation of the clay sample affects the differential temperature curve. These curves are particularly interesting because they show that Ennis and Hufft were successful in at least partially replacing the hydrogen ions. It is also significant to note for the

monovalent cations of the kaolinite and bentonite samples that the magnitude of the reactions decrease in the same order as that of the lyotropic series developed by Hans Jonny (5). This series is not strictly indicated in the illite sample, which is to be expected however, since the magnitudes of the reactions are so small that a difference in the amplitudes was often difficult to detect.

The effect of ion saturation on the differential temperature curve also suggests that the environment in which a clay mineral is weathered would affect a quantitative analysis by the differential thermal method.

Pretreatment of materials to be tested also include drying them at 50° C for at least 24 hours prior to testing. All samples remained in the drying oven at 50° C for the duration of the investigation. Repeated tests on these samples over an extended period of time indicated a gradual decrease in the magnitudes of all reactions. It was thus concluded that leaving the samples in the drying oven for more than 24 hours removes not only the hygroscopic moisture but some of the crystal lattice water as well.

Waight of Sample:

Hudson and Hoskins endeavored to develop

standard differential thermal curves for use in a quantitative analysis. However, since it was not possible to duplicate these standard differential temperature curves with sufficient accuracy for a quantitative analysis, it became necessary to develop a method whereby the quantity of material tested could be accurately controlled.

Two series of tests were conducted to determine the effect of the weight of the active material present in the sample on the thermal curve. In one series of tests, the weight of a kaolinite sample was decreased in 20 percent increments, whereas in the other series of tests the kaolinite was mixed with alumina. Although the total weight of the sample mixture remained the same, the weight of active material in the sample was reduced in the same 20 percent increments. The results of these two series of tests are shown by the first two sets of curves in Appendix E.

The results of this phase of the investigation indicated that a definite correlation exists between the weight of active material present and the magnitudes of the reactions. The curves showing the effect of sample weight were plotted with respect to the zero millivolt line of the

Speedomax and indicate a considerable displacement as the weight of kaolinite decreases. Nevertheless, the magnitudes of reactions measured from the displaced base line of the curve are essentially the same as the magnitudes of the reactions for the same weight of kaolinite mixed with alumina. These series of tests offer further evidence that the amplitude of the peak reactions, measured from the displaced base line, are not affected by the displacement of the thermal curve.

It has been recommended by some investigators (6) that quantitative data could be obtained from differential thermal curves, provided the weights of sample and standard used are proportioned according to their specific heats. From the series of tests described above, it can be concluded that the magnitude of the reactions is dependent only on the quantity of clay sample present and that the ratio of sample weight to standard weight merely affects the displacement of the curve.

Weight Calibration:

Prior to performing a quantitative analysis, it was necessary to determine the relationship between magnitudes of peak reactions and the

percent by weight of a pure clay mineral present in the sample. Differential temperature curves for mixtures of pure clay minerals and alumina are included in Appendix E. These curves were plotted with respect to the base line of the curve. The sample weight used was the maximum which could be conveniently placed in the sample cell.

From these tests a series of calibration curves for each of the three clays were prepared which indicate the relation between the magnitude of the peak reactions and weight of active material present. (Appendix F). It was hoped that these calibration curves could be used to determine the weight of each type of clay present in a mixture of two or more clay minerals.

Mixtures:

Tests were conducted on mixtures of bentonite and kaolinite in which weights of the two minerals were made the same as those used in preparing the calibration curves (Appendix G). Again the magnitudes of the peak reactions, measured from the displaced base line, were plotted as a function of the weight of each clay mineral present in the mixture. Curves showing a comparison of the magnitudes of reactions for known weights of clay in alumina mixtures and mixtures of the two clays are also contained in Appendix G.

An analysis of these curves reveals that the magnitudes of the kaolinite endothermic reaction for the kaolinite-bentonite mixture is consistently lower than the magnitude of the same reaction in the kaolinite-alumina mixture for the same weight of kaolinite present. The curves comparing these reactions are almost parallel and even exhibit the same reversal at 0.5 grams.

The curves showing a comparison of the magnitudes of the kaolinite exothermic reactions indicate that the magnitudes of the exothermic reactions are also considerably lower for the kaolinite-bentonite mixture than for the kaolinito-alumina mixture. These curves also exhibit reversal at 0.5 grams which is more pronounced for the kaolinite-bentonite mixture than for the kaolinite-alumina mixture.

The curves showing a comparison of the magnitudes of the first significant bentonite endothermic reactions for known weights of bentonite in bentonite-kaolinite and bentonite-alumina mixtures indicate that the magnitudes of the reactions for the bentonite-kaolinite mixture are considerably greater than those for the bentonite-alumina mixture. The greatest discrepancy appears to occur at about 0.4 grams where the magnitude of the reaction for the bentonite-kaolinite mixture is nearly twice that of the

reaction for the bentonite-alumina mixture.

Thus, in a mixture of bentonite and kaolinite, the reactions of the kaolinite are lower than those obtained from the calibration curves, while the bentonite reactions are considerably higher.

From this investigation it can be concluded that the thermal characteristics of a mixture of active clay minerals are different from those of clay-alumina mixtures. It is reasonable to assume that these differences are due to changes in both the mean thermal conductivity and mean heat capacity of the clay mixtures. Furthermore, these changes in the thermal characteristics are not constant but vary with the proportion of active materials present. A quantitative differential thermal analysis which does not consider the difference between the thermal characteristics of a mixture of active materials and a synthetic mixture of a pure clay mineral and alumina can not depend on accuracies of more than 50 percent.

It is regretted that time did not permit a more thorough investigation of this phenomenon.

Summary

In conclusion it can be stated that a considerable number of factors influence the shape of the differential temperature curve. The success of an accurate quantitative differential thermal analysis depends not only upon a full evaluation of these effects but upon their rigorous control as well.

In addition, this investigation has demonstrated that there is a need for further investigation and evaluation of a quantitative analysis by the differential thermal method.

It is hoped that this work has contributed to the need for research in this field.

COMMENTS AND RECOMMENDATIONS

In general, it is believed that the procedures, techniques and equipment used by Hudson and Hoskins in their study on differential thermal analysis is suitable for a qualitative analysis of unknown clay specimens and that their results can be duplicated by other investigators. However, it is believed that certain modifications should be made in the procedures and equipment before an attempt is made to make a quantitative analysis of unknown clay minerals. These modifications are outlined below.

Heating Rate: In order to obtain a more uniform heating rate as well as one which is more consistent with the temperature control mechanism, it is recommended that the two 1000-watt furnaces be converted to 1750-watt furnaces. It will be necessary to carefully calibrate these furnaces in order to eliminate the difficulties described in Appendix H.

Grain Size: In order to be able to obtain a sufficient quantity of active material from an unknown sample for test purposes, it is recommended that future tests on differential thermal curves for pure clays be made on 200-pan grain sizes. It has been found that the use of this grain size gives convenient quantities of active

is hereby notified that the Government of the United States of America is conducting a security investigation of the activities of the Communist Party, U.S.A., and its agents, and that it is in the interest of the national defense that the activities of the Communist Party, U.S.A., and its agents be kept confidential. It is further stated that the Government of the United States of America is conducting a security investigation of the activities of the Communist Party, U.S.A., and its agents, and that it is in the interest of the national defense that the activities of the Communist Party, U.S.A., and its agents be kept confidential.

It is the policy of the Government of the United States of America to protect the national defense by keeping confidential the activities of the Communist Party, U.S.A., and its agents. It is further stated that the Government of the United States of America is conducting a security investigation of the activities of the Communist Party, U.S.A., and its agents, and that it is in the interest of the national defense that the activities of the Communist Party, U.S.A., and its agents be kept confidential.

It is the policy of the Government of the United States of America to protect the national defense by keeping confidential the activities of the Communist Party, U.S.A., and its agents. It is further stated that the Government of the United States of America is conducting a security investigation of the activities of the Communist Party, U.S.A., and its agents, and that it is in the interest of the national defense that the activities of the Communist Party, U.S.A., and its agents be kept confidential.

material for each of the three clays tested.

It is further recommended that this grain size be used for the standard in order to obtain the most consistent results.

Pretreatment: It has been found that many factors used in treating a clay specimen prior to testing determines, to a large extent, the shape of the differential thermal curve. It is desired to emphasise the necessity for uniform pretreatment of all clays to be tested if a quantitative analysis is to be attempted. Standard differential thermal curves prepared for pure clays receiving one type of pretreatment may not compare with other differential thermal curves obtained from the same pure clays which received a slightly different pretreatment. It is recommended that clays to be tested be oven-dried at a temperature of 50° C for a period of 24 hours. Oven drying for longer periods of time tends to reduce crystal-lattice water and therefore reduces the magnitudes of the thermal reactions.

Ion Saturation: The influence of ion saturation on the differential thermal curves has been discussed in the section on Results and Conclusions. It is recommended that further quantitative work on this subject be accomplished in order to determine the extent of the influence

of this factor on differential thermal curves.

Weight of Material: Since the magnitude of the reaction is a direct function of the weight of the active material present in the sample, it is recommended that future differential thermal tests be made on the basis of measured weights of the sample. It is further recommended that the weight of the standard be identical with that of the sample in order to reduce displacement of the base line. It has been found as a result of this investigation that a change in the weight ratio merely serves to shift the base line of the differential thermal curve and does not effect the magnitude of the reaction which is dependent only on the weight of the active material present. In addition, there is no evidence to indicate that the specific heats of the two materials changes at a constant rate with temperature change. Therefore, it is believed that using weight ratios based on specific heats would not serve a useful purpose in quantitative analysis of clays.

Conductivity: In the section on the Results and Conclusions it was pointed out that the differences in conductivity between the sample and the standard results in a displacement of the base line but does not effect the amplitude

of the reactions for a given weight of active material. In order to achieve the most consistent results for a quantitative analysis it is recommended that the base line of the curve be used in measuring the amplitude of the reaction. In addition it is recommended that tests be made to determine the effects on the differential thermal curve by using constant weights of material but varying the grain size of the sample and standard.

Magnification of Amplitude: In order to permit a more detailed analysis of the magnitude of the smaller reactions of bentonites and illites, it is recommended that the Speedomax circuit be modified to provide a choice of amplification scales. It is believed that this modification would require neither an extensive nor expensive alteration of the existing equipment and that such a choice of scales would permit a more sensitive analysis of significant reaction magnitudes.

REFERENCES

- (1) Kerr, P.F., and Kulp, J. L.
"Multiple Differential Thermal Analysis."
The American Mineralogist, Vol. 33, July -
August 1943.
- (2) Grim, R.E., and Rowland, R.A.
"Differential Thermal Analysis of Clay
Minerals and Other Hydrous Materials"
The American Mineralogist, Vol. 27, 1942
- (3) Page, J.B.
"Differential Thermal Analysis of Mont-
morillonite"
Soil Science, Vol. 56, 1943
- (4) Ennis, W.D., and Hufft, J.C.
"Investigation of the Effect of Various
Cations on the Atterberg Limits of Kaolinite,
Illite, and Montmorillonite."
Ronselaer Polytechnic Institute, 1951.
- (5) Jenny, Hans
"Mechanism of Ionic Exchange in Colloidal
Aluminum Silicates."
Journal of Physical Chemistry, Vol. 36,
Part 2, 1932
- (6) Jeffries, C.D.
"A Quantitative Approach to the Study of
the Thermal Characteristics of Clays."
Soil Science Society of America, Proceedings,
1944.
- (7) Grim, R.E. and Bradley, W.F.
"Rehydration and Dehydration of the Clay
Minerals."
The American Mineralogist, Vol.33, Jan-
Feb. 1948.
- (8) Faust, G.T.
"Thermal Analysis of Quartz and Its use in
Calibration in Thermal Analysis Studies."
The American Mineralogist, Vol.33, May-June
1948.
- (9) Speil, S., Berkolhamer, L.H., Pask, J.A., and
Davis, B.
"Differential Thermal Analysis, Its Applica-
tion to Clay and Other Aluminous Minerals."
U.S. Bureau of Mines, Technical Paper
664, 1945

- (10) Norton, F. H.
"Initial Study of the Differential Thermal
Method for the Identification of the Clay
Minerals."
Journal, American Ceramic Society,
Vol. 22, 1939.
- (11) Hondricks, S.B., Nelson, R.A., and Alexander, L.T.
"Hydrated Mechanism of the Clay Mineral
Montmorillonite Saturated with Various
Cations."
Journal, American Chemical Society,
Vol. 62, 1940.
- (12) Insley, H., and Ewell, R.H.
"Thermal Behavior of Kaolin Minerals."
Journal of Research, U.S. Bureau of
Standards, Vol. 14, 1935.
- (13) Grim, R.E., and Bradley, W.F.
"Investigation of the Effect of Heat on the
Clay Minerals Illite and Montmorillonite."
Journal, American Ceramic Society,
Vol. 23, 1940.
- (14) Norton, F.H.
"Analysis of High-Alumina Clays by the
Thermal Method."
Journal, American Ceramic Society, Vol.
23, 1940.
- (15) Gruver, R.M.
"Precision Method of Thermal Analysis."
Journal, American Ceramic Society, Vol. 31, 1948.
- (16) Hendricks, S.B., Goldrich, S.S., and Nelson, R.A.
"A Portable Differential Thermal Outfit."
Economic Geology, Vol. 41
- (17) Grim, R.E.
"Differential Thermal Curves of Prepared
Mixtures of Clay Minerals."
The American Mineralogist, Vol. 32, 1947.
- (18) Cuthbert, F.L., and Rowland, R.A.
"Differential Thermal Analysis of Some
Carbonate Minerals."
The American Mineralogist, Vol. 32, 1947.

- (19) Beck, C. W.
"An Improved Method of Differential Thermal Analysis and Its Use in the Study of the Natural Carbonates."
Harvard University Ph.D. Thesis.
- (20) Vold, M.J.
"Differential Thermal Analysis."
Analytical Chemistry, Vol.21, No. 6
- (21) Grim, R.E., and Rowland, R.A.
"Differential Thermal Analysis of Clays and Shales; A Control and Prospecting Method."
Journal, American Ceramic Society,
Vol. 27., 1944.
- (22) Allaway, W.H.
"Differential Thermal Analysis of Clays Treated with Organic Cations as an Aid in the Study of Soil Colloids."
Soil Science of America, Proceedings.
Vol. 13, 1948.
- (23) Kerr, P.F., Kulp, J.L., and Hamilton, P.K.
"Differential Thermal Analysis of Reference Clay Mineral Specimens."
American Petroleum Institute, Project
49, Preliminary Report No. 3, 1949

APPENDIXES

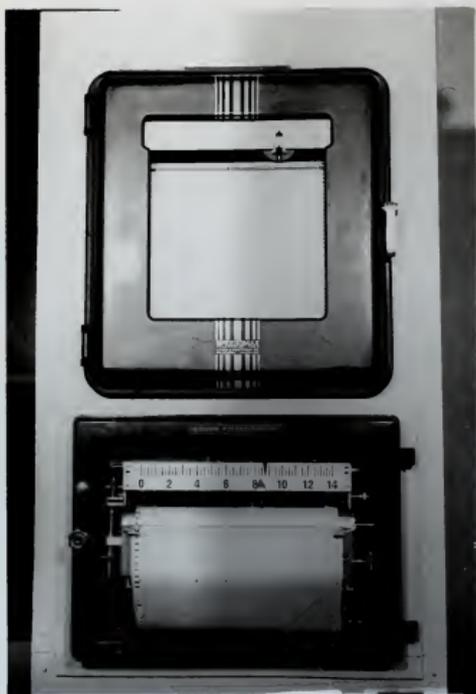
- A. PHOTOGRAPHS OF EQUIPMENT AND A CIRCUIT DIAGRAM.
- B. RECORD OF TESTS CONDUCTED
- C. GRAIN SIZE STUDIES
- D. EFFECTS OF PRETREATMENT
- E. EFFECT OF SAMPLE WEIGHT
- F. WEIGHT CALIBRATION
- G. MIXTURES
- H. DISCUSSION OF 1750 WATT FURNACE

APPENDIX A

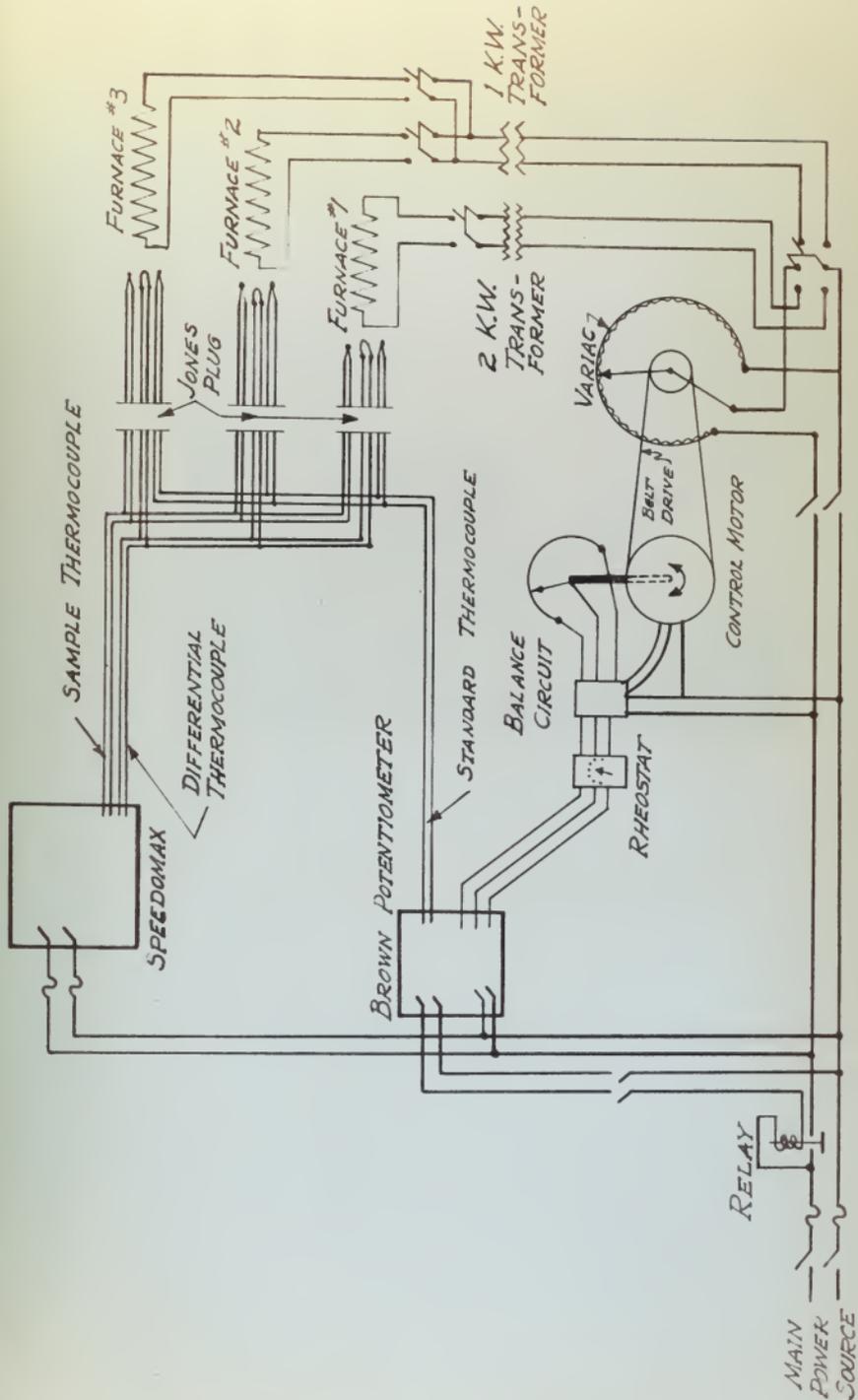
1. PHOTOGRAPH OF TEST EQUIPMENT
2. PHOTOGRAPH OF RECORDING EQUIPMENT
3. CIRCUIT DIAGRAM
4. PHOTOGRAPH OF SAMPLE HOLDER
5. DETAIL DRAWING OF SAMPLE HOLDER



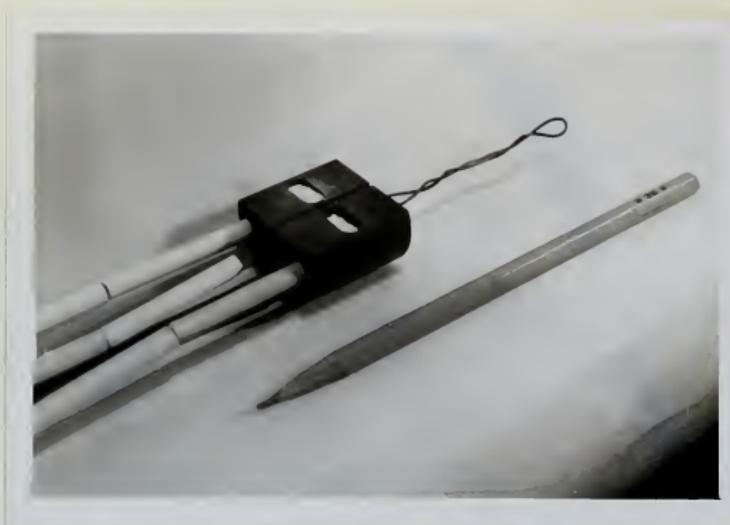
PHOTOGRAPH OF EQUIPMENT



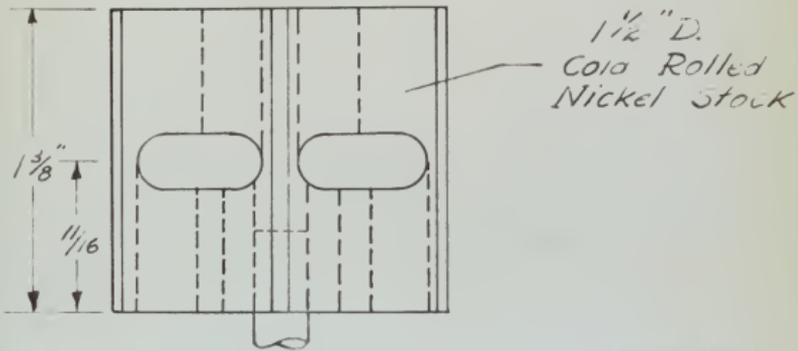
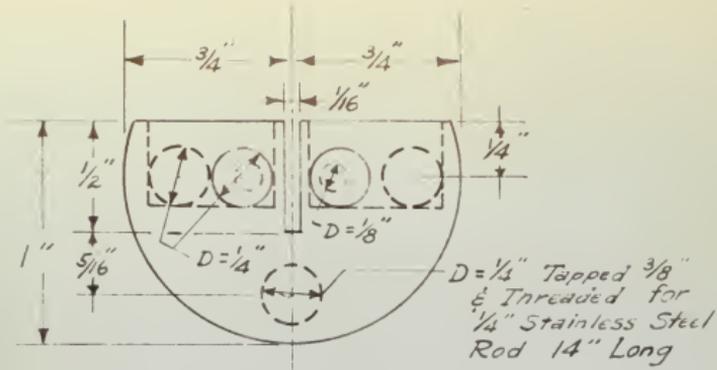
PHOTOGRAPH OF RECORDING APPARATUS



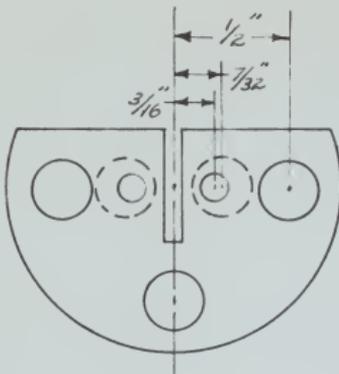
CIRCUIT DIAGRAM ~ DIFFERENTIAL THERMAL ANALYSIS



PHOTOGRAPH OF SAMPLE HOLDER



Scale $\frac{1}{2}$ " = 1"



DETAIL DRAWING FOR SAMPLE HOLDER

APPENDIX B

RECORD OF TESTS CONDUCTED

RECORD OF TEST CONDUCTED

I. Grain Size Studies:

| Clay | Grain Size | No. of Tests |
|-----------|------------|--------------|
| Kaolinite | 100-140 | 3 |
| | 140-200 | 3 |
| | 200-pan | 5 |
| Bentonite | 100-140 | 2 |
| | 140-200 | 3 |
| | 200-pan | 3 |
| Illite | 100-140 | 9 |
| | 140-200 | 7 |
| | 200-pan | 8 |

II. Pretreatment Effects on Illite (140 - 200 Mesh)

| Treatment | No. of Tests |
|--|--------------|
| As Received | 2 |
| Oven Dried | 6 |
| Dispersed in H ₂ O | 2 |
| Treated with H ₂ O | 3 |
| Treated with H ₂ O ₂ and HCl | 2 |

III. Effect of Weight of Sample (140 - 200 Mesh)

| Clay | Wt. | Standard | Wt. | No. of Tests |
|-----------|------|----------|------|--------------|
| Kaolinite | 0.70 | Alumina | 0.70 | 6 |
| | 0.56 | | 0.70 | 5 |
| | 0.42 | | 0.70 | 3 |
| | 0.28 | | 0.70 | 2 |
| | 0.14 | | 0.70 | 2 |

IV. Effect of Weight Ratio of Synthetic Mixture (140-200 Mesh)

| Clay | Sample Mixture | | Standard | No. of Tests |
|-----------|----------------|-------------|----------|--------------|
| | Wt. | Alumina Wt. | Wt. | |
| Kaolinite | 0.70 | 0.00 | 0.70 | 6 |
| | 0.56 | 0.14 | 0.70 | 3 |
| | 0.42 | 0.28 | 0.70 | 3 |
| | 0.28 | 0.42 | 0.70 | 3 |
| | 0.14 | 0.56 | 0.70 | 2 |
| Bentonite | 1.00 | 0.00 | 1.00 | 2 |
| | 0.80 | 0.20 | 1.00 | 2 |
| | 0.60 | 0.40 | 1.00 | 2 |
| | 0.40 | 0.60 | 1.00 | 2 |
| Illite | 0.20 | 0.80 | 1.00 | 2 |
| | 0.80 | 0.00 | 0.80 | 3 |
| | 0.64 | 0.16 | 0.80 | 4 |
| | 0.48 | 0.32 | 0.80 | 3 |
| | 0.32 | 0.48 | 0.80 | 3 |

V. Effects of Ion Saturation (140 - 200 Mesh)

| Clay | Ion | No. of Tests |
|-----------|-----------|--------------|
| Kaolinite | Hydrogen | 3 |
| | Calcium | 2 |
| | Potassium | 2 |
| | Sodium | 2 |
| Bentonite | Hydrogen | 2 |
| | Calcium | 2 |
| | Potassium | 2 |
| | Sodium | 2 |
| Illite | Hydrogen | 6 |
| | Calcium | 4 |
| | Potassium | 4 |
| | Sodium | 6 |

VI. Effect of Ratio of Weight of Sample to Weight of Standard (140 - 200 Mesh)

| Sample | Wt. | Standard | Wt. | Ratio | No. of Tests |
|-----------|-------|----------|-------|-------|--------------|
| Kaolinite | 0:50 | Alumina | 0.50 | 1:1 | 1 |
| | 0.26 | | 0.50 | 1:2 | 2 |
| | 0:50 | | 1.00 | 1:2 | 5 |
| | 1.00 | | 1.00 | 1:1 | 1 |
| Bentonite | 0:50 | Alumina | 0.50 | 1:1 | 1 |
| | 1.00 | | 1.00 | 1:1 | 1 |
| Kaolinite | 0.775 | Alumina | 0.775 | 1:1 | 1 |
| Bentonite | 0.75 | Alumina | 1.00 | 3:4 | 1 |

VII. Study of Clay Mixtures (140 - 200 Mesh)

| Clay | Sample | | Standard Wt. | No. of Tests | |
|-----------|--------|-----------|--------------|--------------|-----|
| | Wt. | Clay | | | Wt. |
| Kaolinite | 0.28 | Bentonite | 0.60 | 0.77 | 3 |
| | 0.28 | | 0.40 | 0.68 | 4 |
| | 0.42 | | 0.40 | 0.82 | 2 |
| | 0.48 | | 0.40 | 0.88 | 1 |
| | 0.50 | | 0.20 | 0.70 | 1 |
| | 0.56 | | 0.20 | 0.70 | 3 |

VIII. Miscellaneous Tests

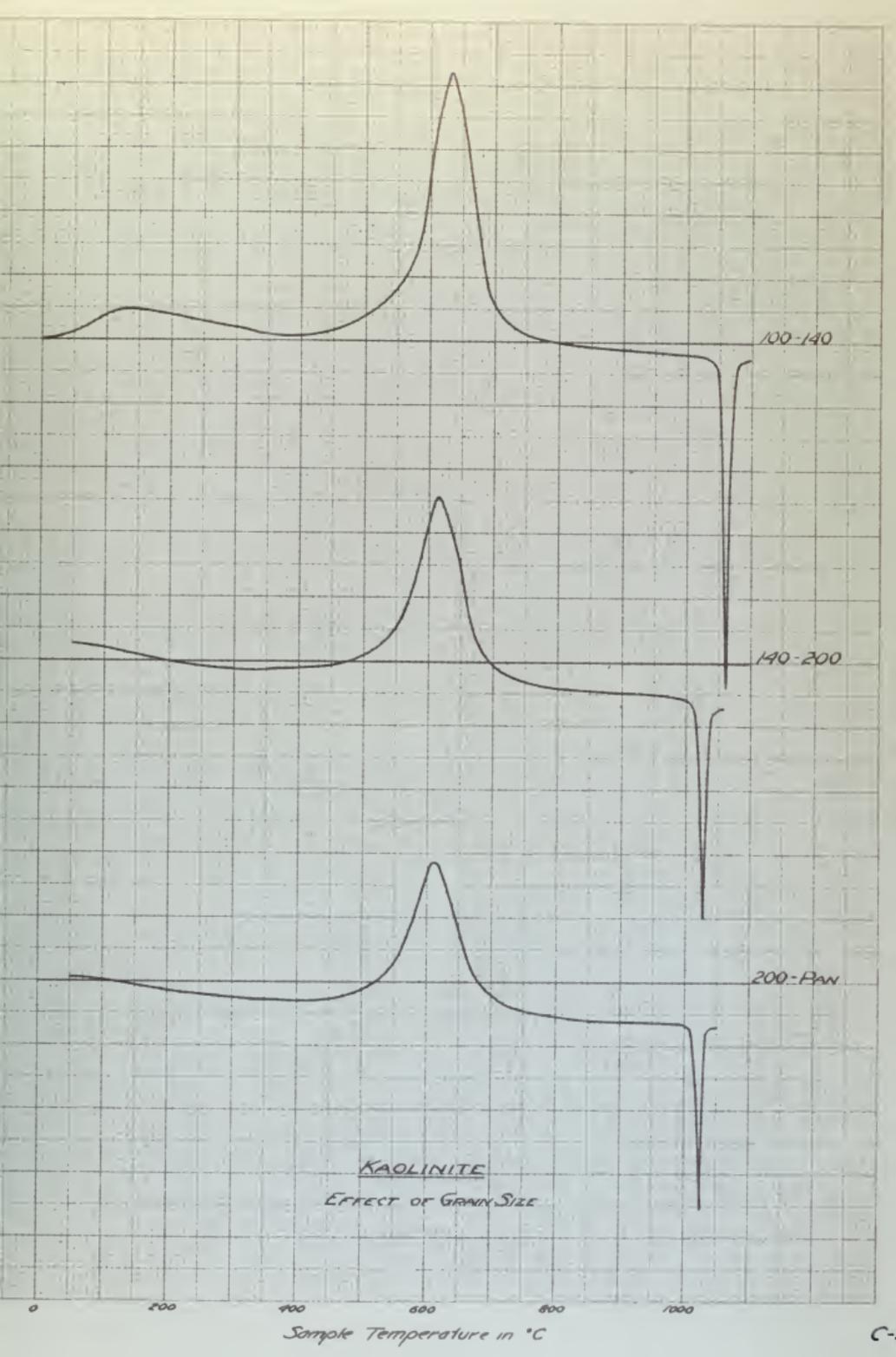
| Type of Test | No. of Tests |
|--|--------------|
| Differential Thermal Checks | 11 |
| Check on 1750 Watt Furnace | 18 |
| Use of Calcined Kaolin as Standard | 1 |
| Conductivity Test (Alumina in Sample and Standard) | 4 |
| Tests on Varved Clays | 3 |

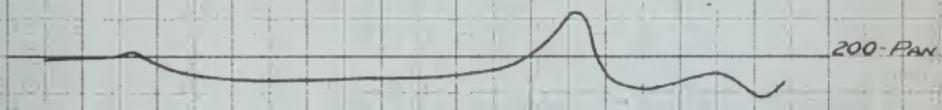
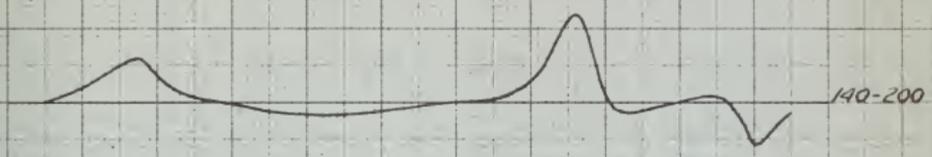
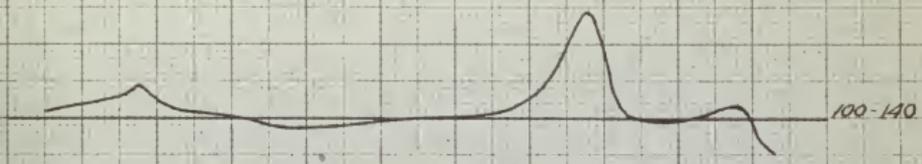
NOTE: All weights are measured in Grams.

APPENDIX C

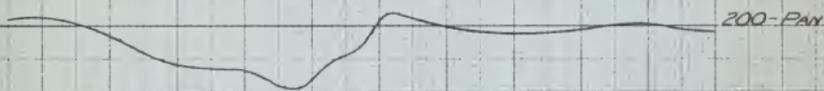
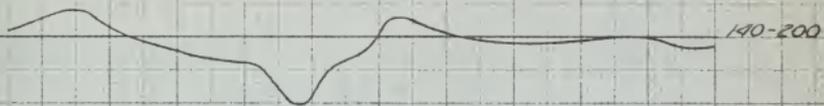
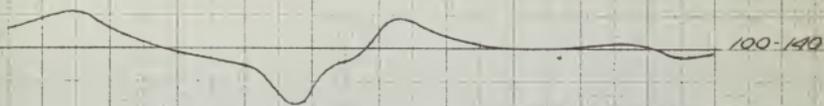
EFFECT OF VARIATION IN GRAIN SIZE ON THE
DIFFERENTIAL THERMAL CURVE

1. Kaolinite
2. Bentonite
3. Illite





BENTONITE
EFFECT OF GRAIN SIZE



ILLITE
EFFECT OF GRAIN SIZE
(DISPERSED IN DISTILLED WATER)

0 200 400 600 800 1000

Sample Temperature in °C

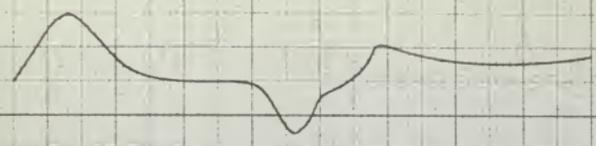
1" = 0.40 Millivolts

APPENDIX D

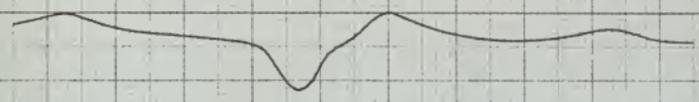
EFFECT OF PRETREATMENT ON THE DIFFERENTIAL THERMAL CURVE

1. Pretreatment of Illite
2. Effect of Ion Saturation on Kaolinite
3. Effect of Ion Saturation on Bentonite
4. Effect of Ion Saturation on Illite

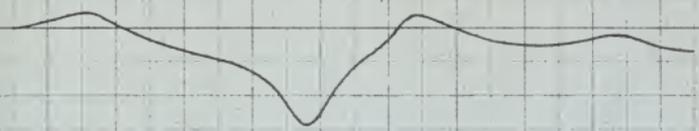
1" = 0.90 Millivolts



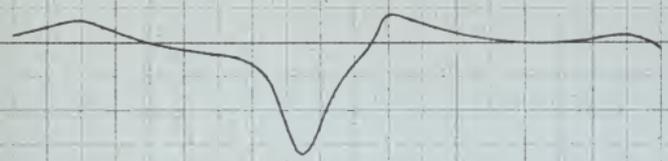
As Received



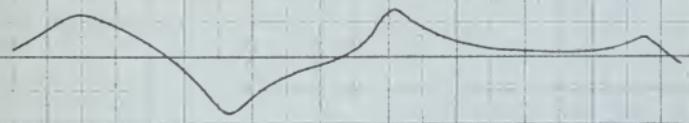
Oven Dried
24 hours at
50°C



Dispersed in
distilled H₂O
Oven Dried



Dispersed
Treated with
H₂O₂
Oven Dried

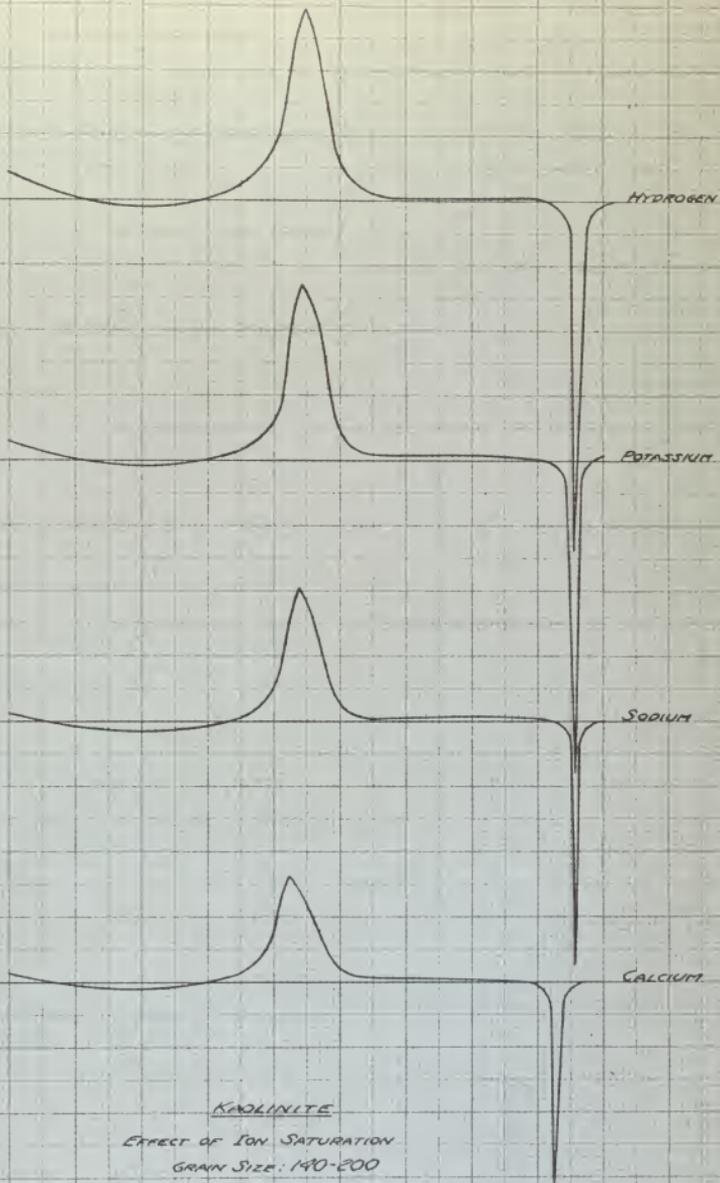


Dispersed
Treated with
H₂O₂ + HCl
Oven Dried

ILLITE
GRAIN SIZE: 140-200
EFFECT OF PRE-TREATMENT

0 200 400 600 800 1000

Sample Temperature in °C



1" = 0.40 Millivolts

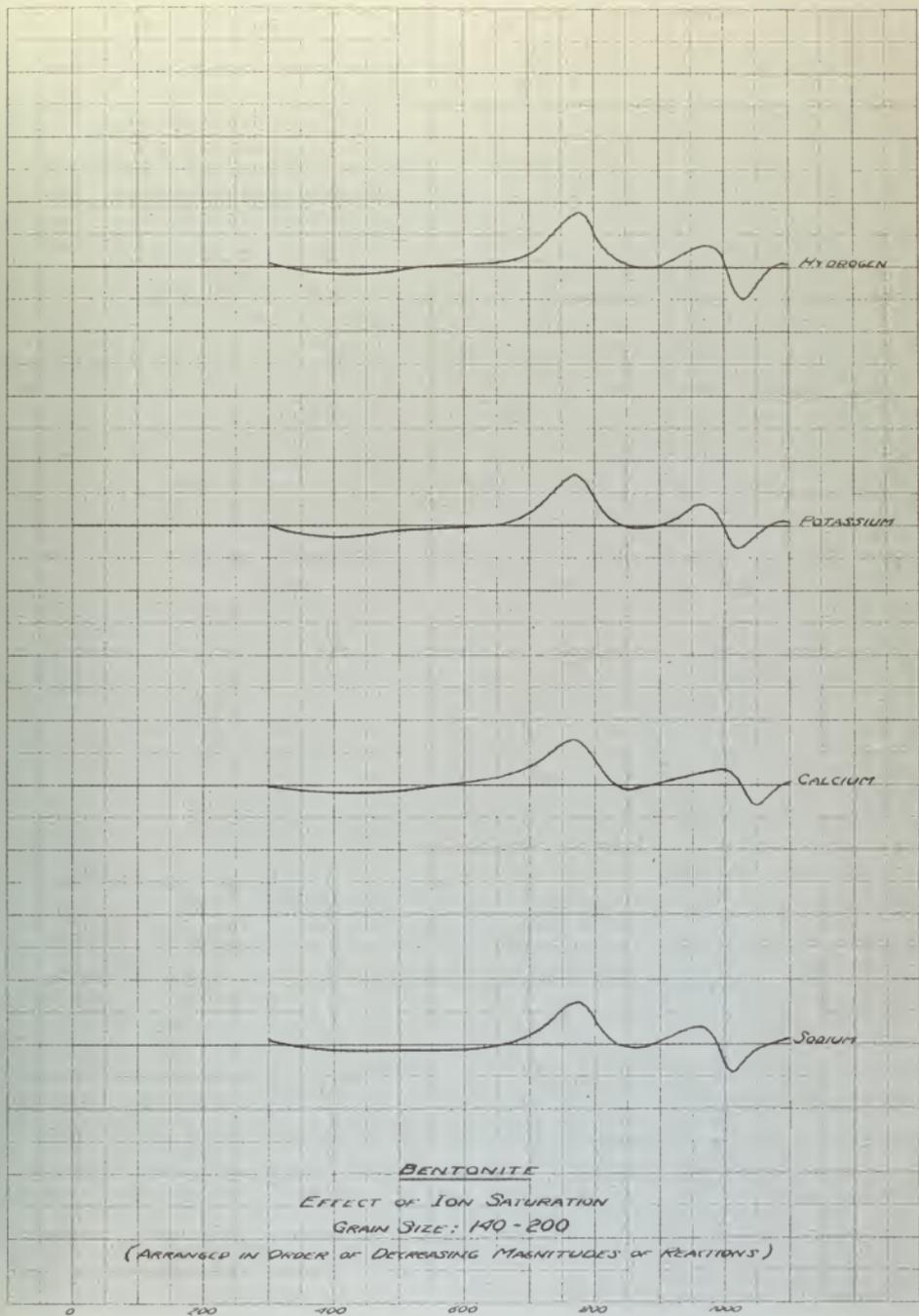
KAOHLINITE

EFFECT OF ION SATURATION
GRAIN SIZE: 140-200

(ARRANGED IN ORDER OF DECREASING MAGNITUDES OF REACTIONS)

0 200 400 600 800 1000

Sample Temperature in °C



1" = 0.40 MILLIGRAMS

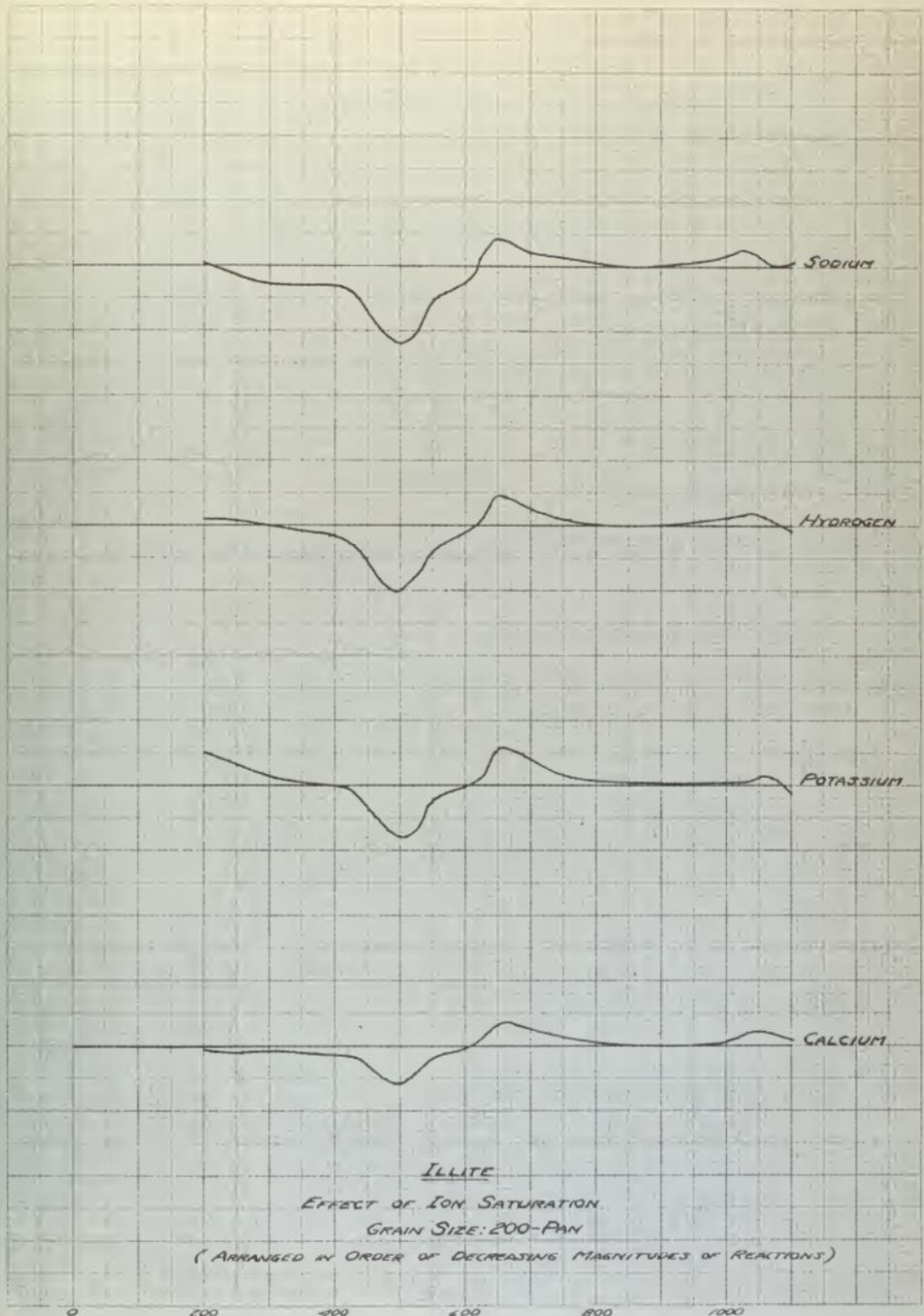
BENTONITE

EFFECT OF ION SATURATION

GRAIN SIZE: 140-200

(ARRANGED IN ORDER OF DECREASING MAGNITUDES OF REACTIONS)

Sample Temperature in °C



1" = 0.40 Millivolts

ILLITE

EFFECT OF ION SATURATION.

GRAIN SIZE: 200-PAN

(ARRANGED IN ORDER OF DECREASING MAGNITUDES OF REACTIONS)

Sample Temperature in °C

APPENDIX E

EFFECT OF SAMPLE WEIGHT ON THE DIFFERENTIAL THERMAL CURVE

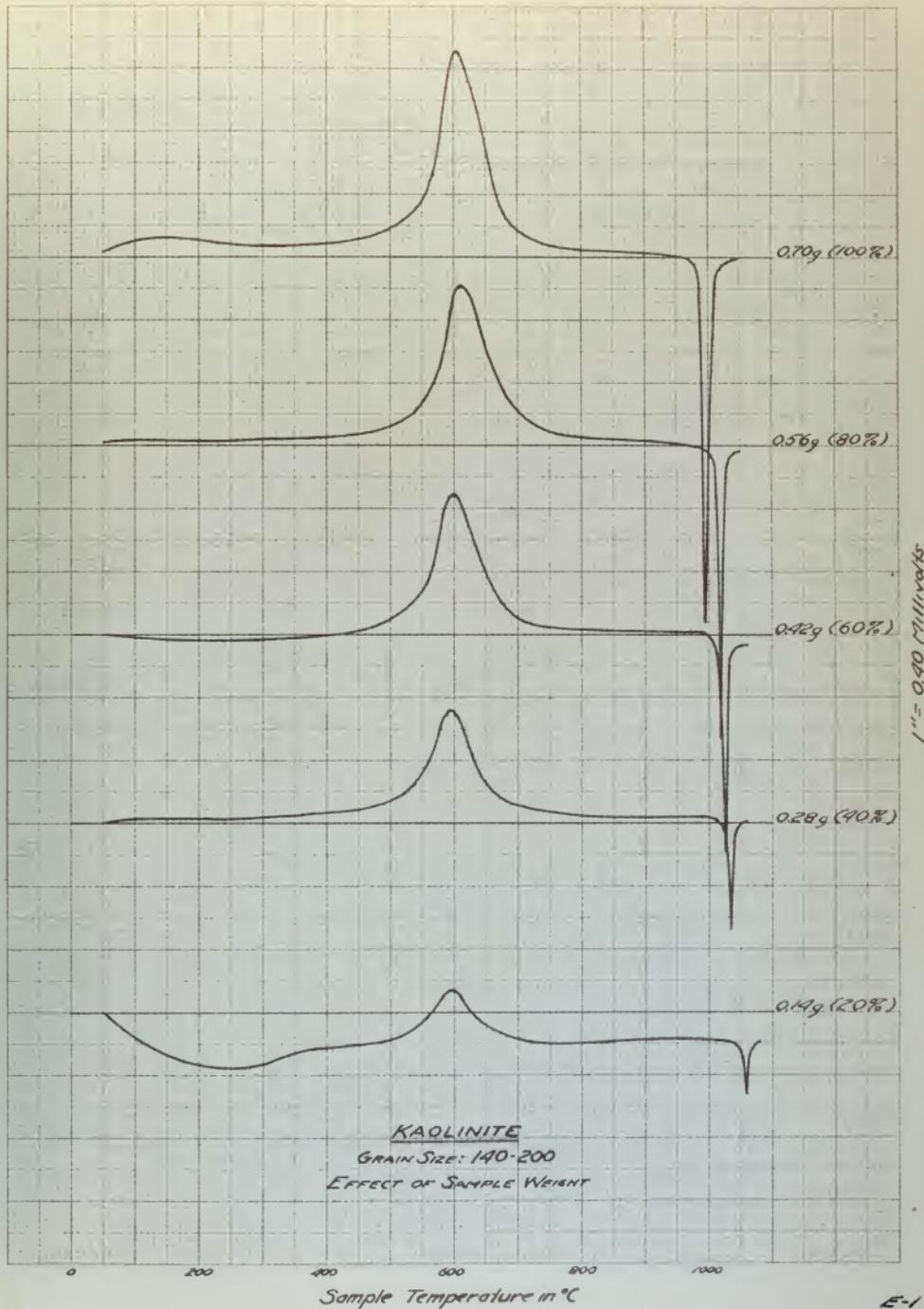
1. Sample Weight of Kaolinite
2. Mixture of Kaolinite and Alumina
3. Mixture of Bentonite and Alumina
4. Mixture of Illite and Alumina

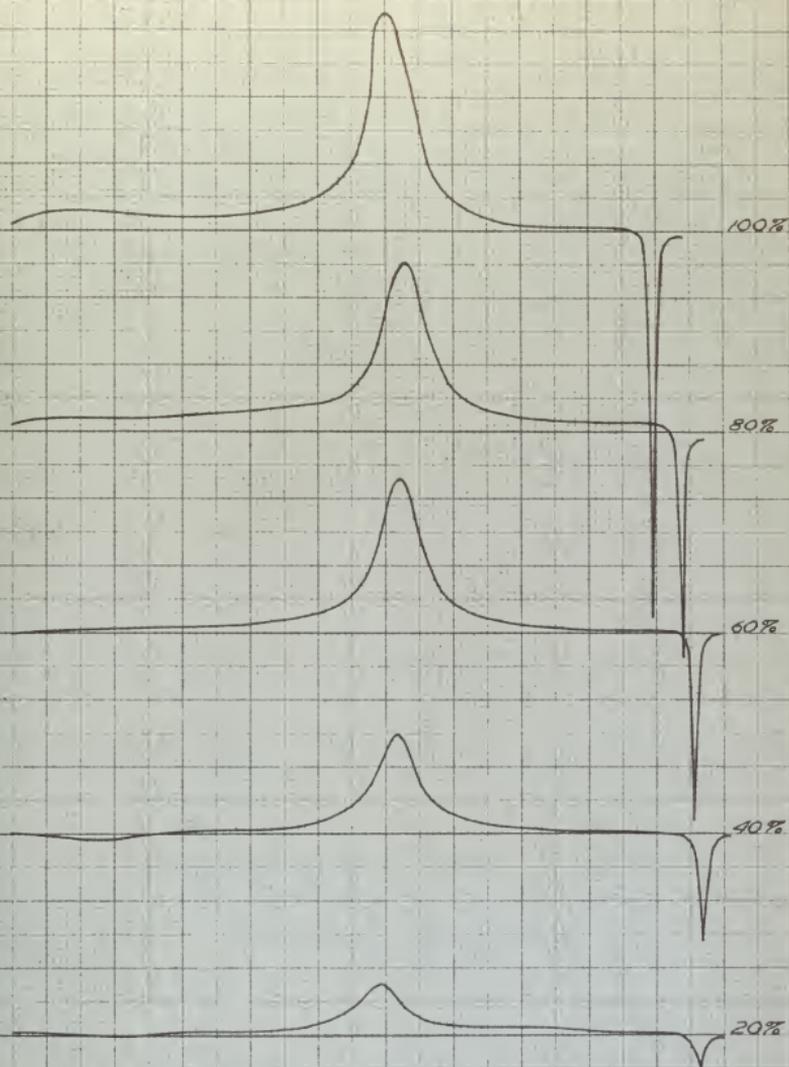
7

THESE ARE THE RESULTS OF THE RESEARCH WORK

- 1. THE RESEARCH WORK
- 2. THE RESEARCH WORK
- 3. THE RESEARCH WORK
- 4. THE RESEARCH WORK

•
•
•



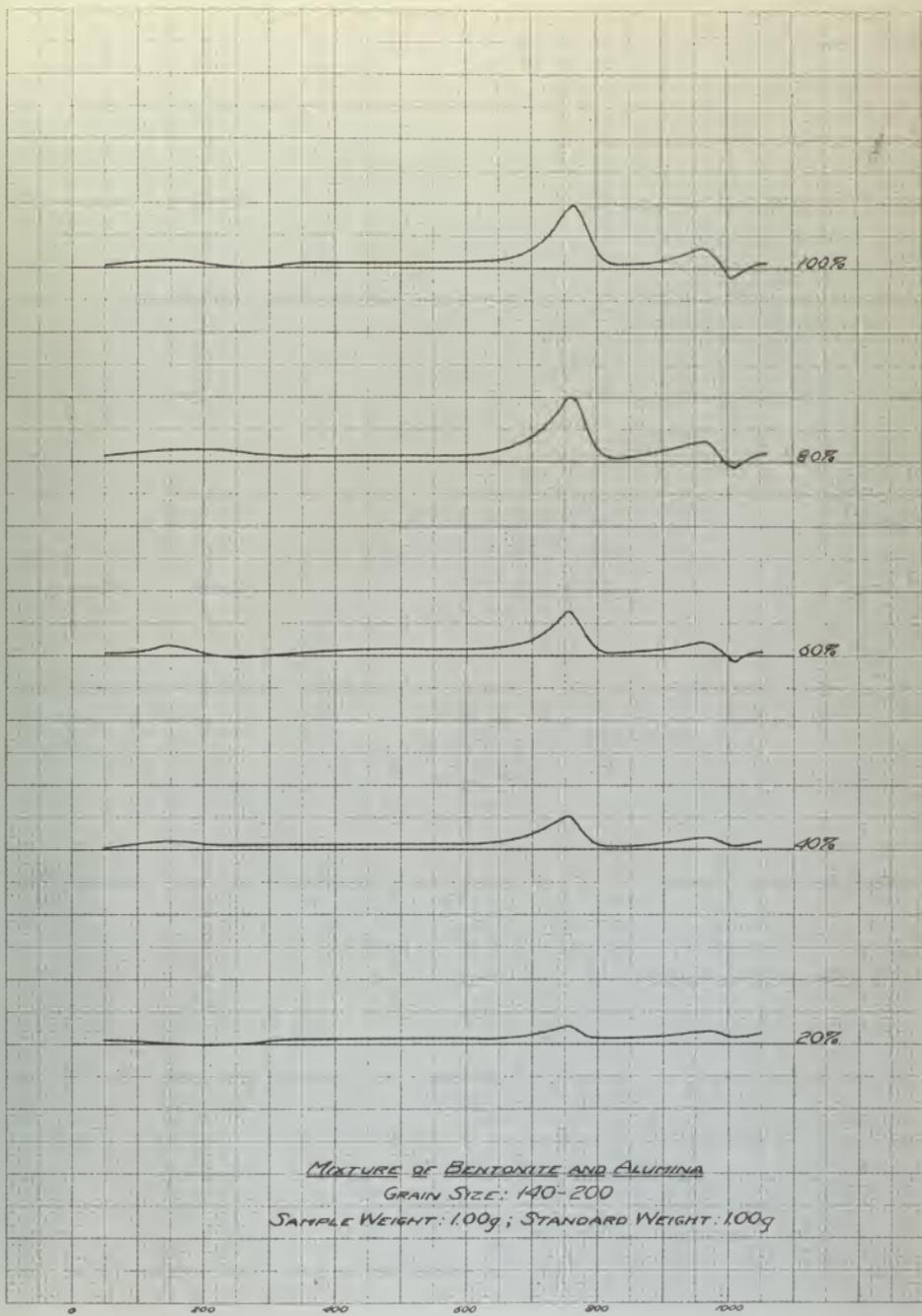


1" = 0.40 Millivolts

MIXTURE OF KAOLINITE AND ALUMINA
GRAIN SIZE: 140-200
SAMPLE WEIGHT: 0.70g; STANDARD WEIGHT: 0.70g

0 200 400 600 800 1000

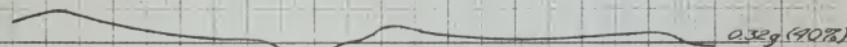
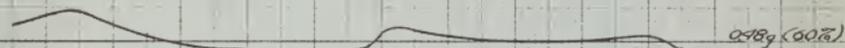
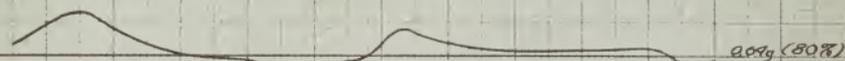
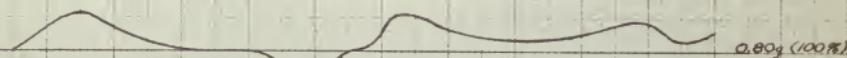
Sample Temperature in °C



1'' = 0.40 Millivolts

MIXTURE OF BENTONITE AND ALUMINA
 GRAIN SIZE: 140-200
 SAMPLE WEIGHT: 1.00g; STANDARD WEIGHT: 100g

Sample Temperature in °C



MIXTURE OF ILLITE AND ALUMINA
GRAN SIZE: 170-200
STANDARD WEIGHT - 0.80g

Sample Temperature in °C

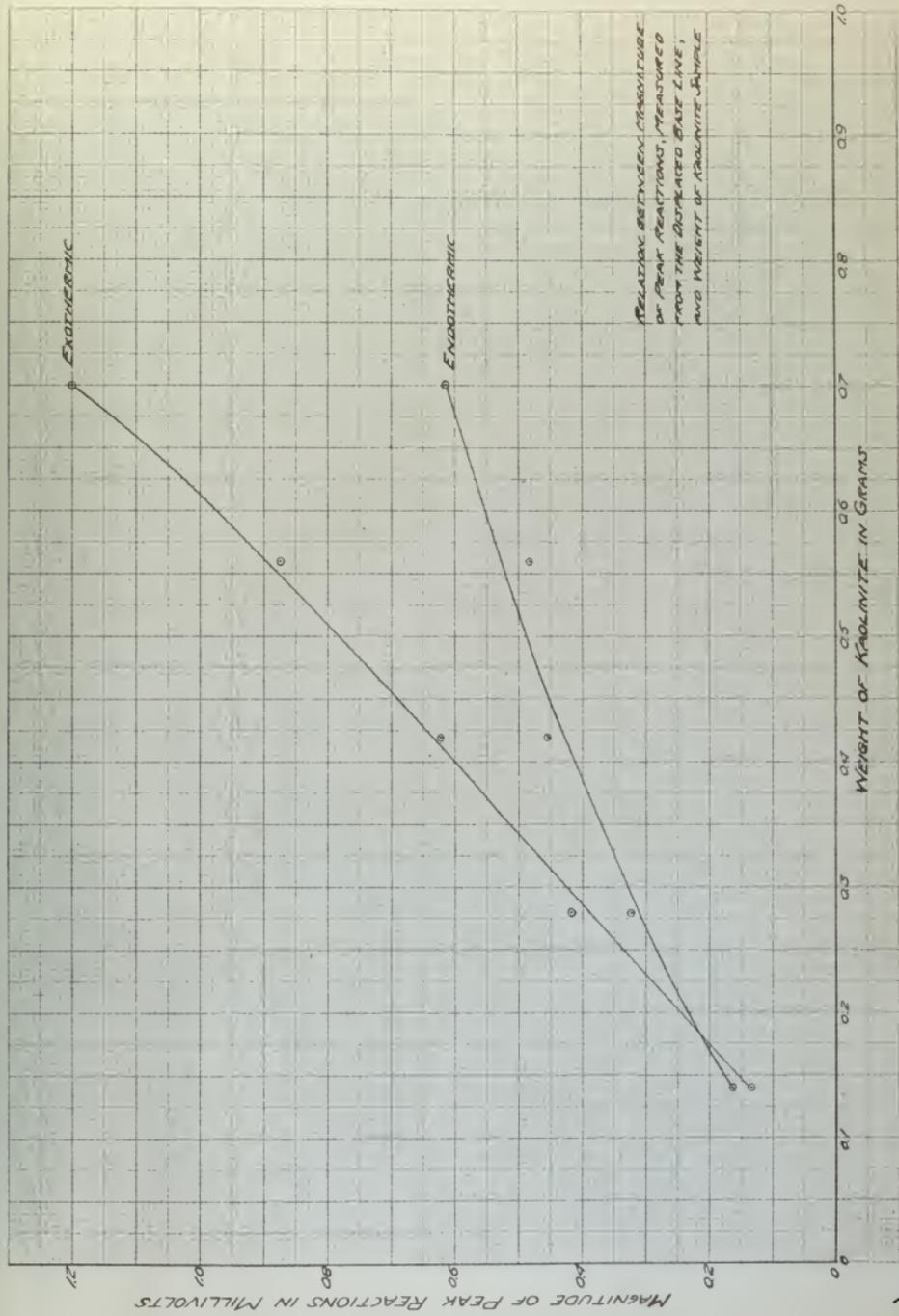
1" = 0.40 Millivolts

APPENDIX F

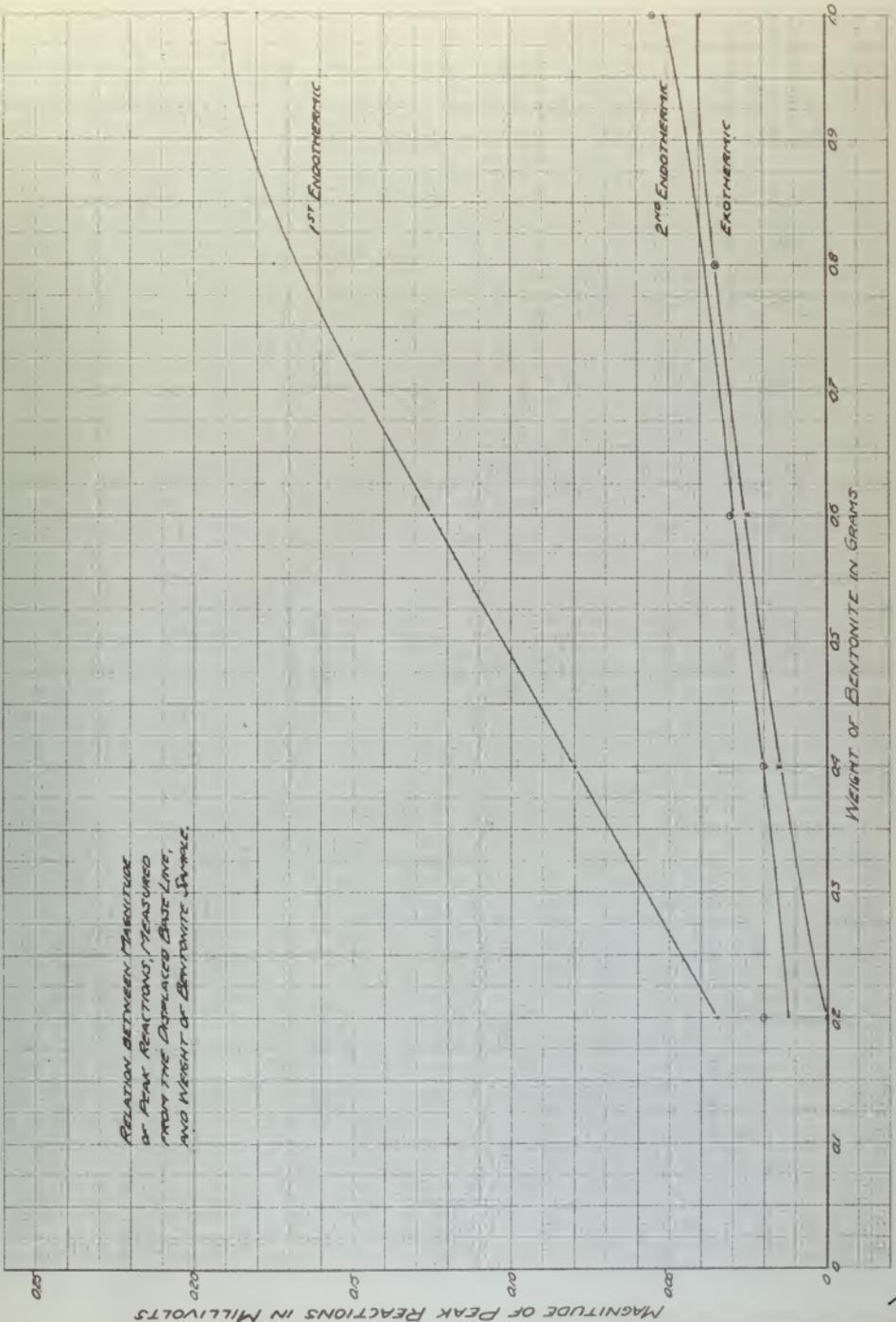
1. CALIBRATION CURVE FOR KAOLINITE
2. CALIBRATION CURVE FOR BENTONITE
3. CALIBRATION CURVE FOR ILLITE

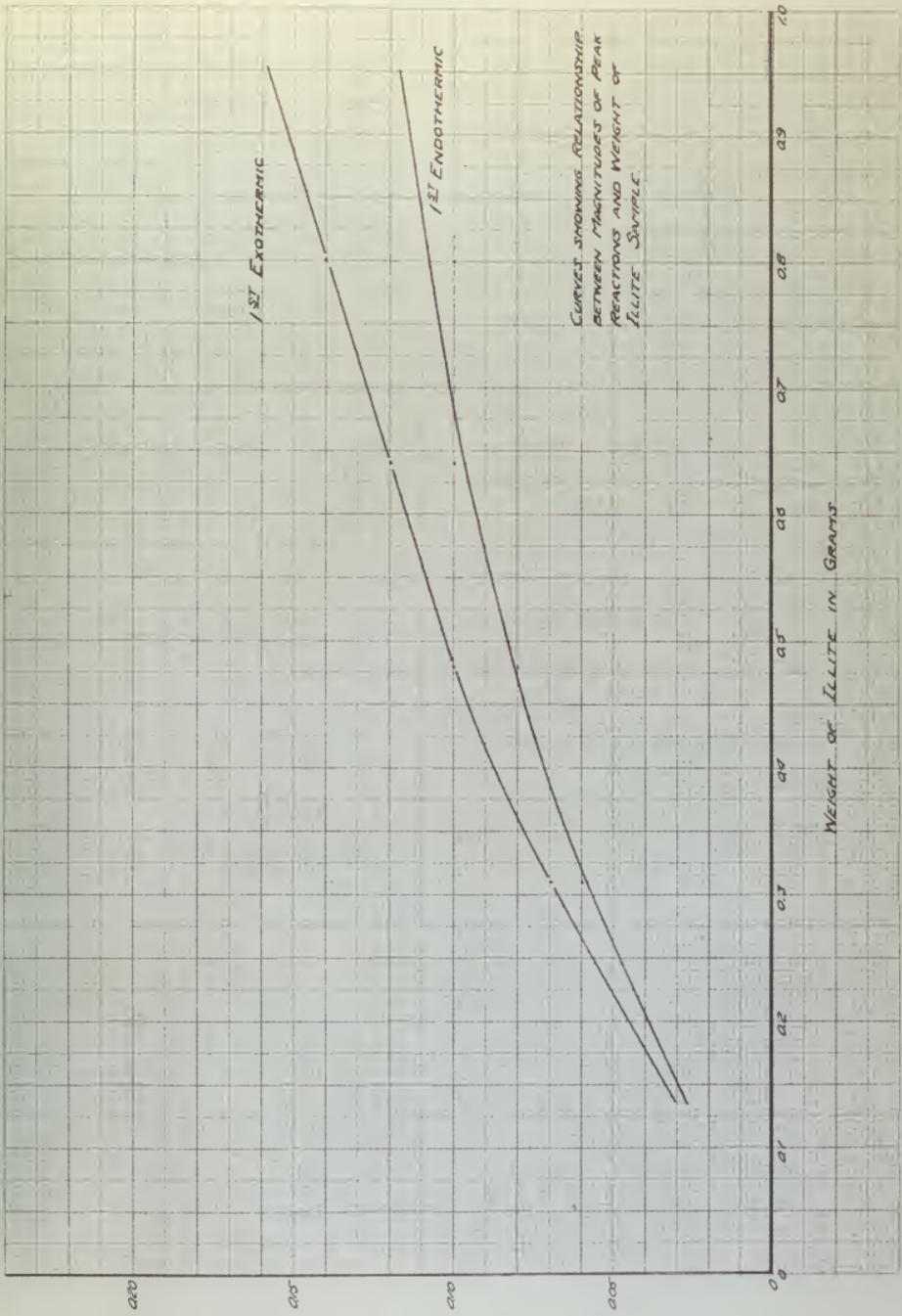
TABLE

| | |
|-------------|---|
| CHAPTER I | 1 |
| CHAPTER II | 1 |
| CHAPTER III | 1 |



RELATION BETWEEN MAGNITUDE
OF PEAK REACTIONS, MEASURED
FROM THE DEPLETED BLUE LINE,
AND WEIGHT OF BENTONITE SAMPLE.





CURVES SHOWING RELATIONSHIP BETWEEN MAGNITUDES OF PEAK REACTIONS AND WEIGHT OF ILLITE SAMPLE.

APPENDIX G

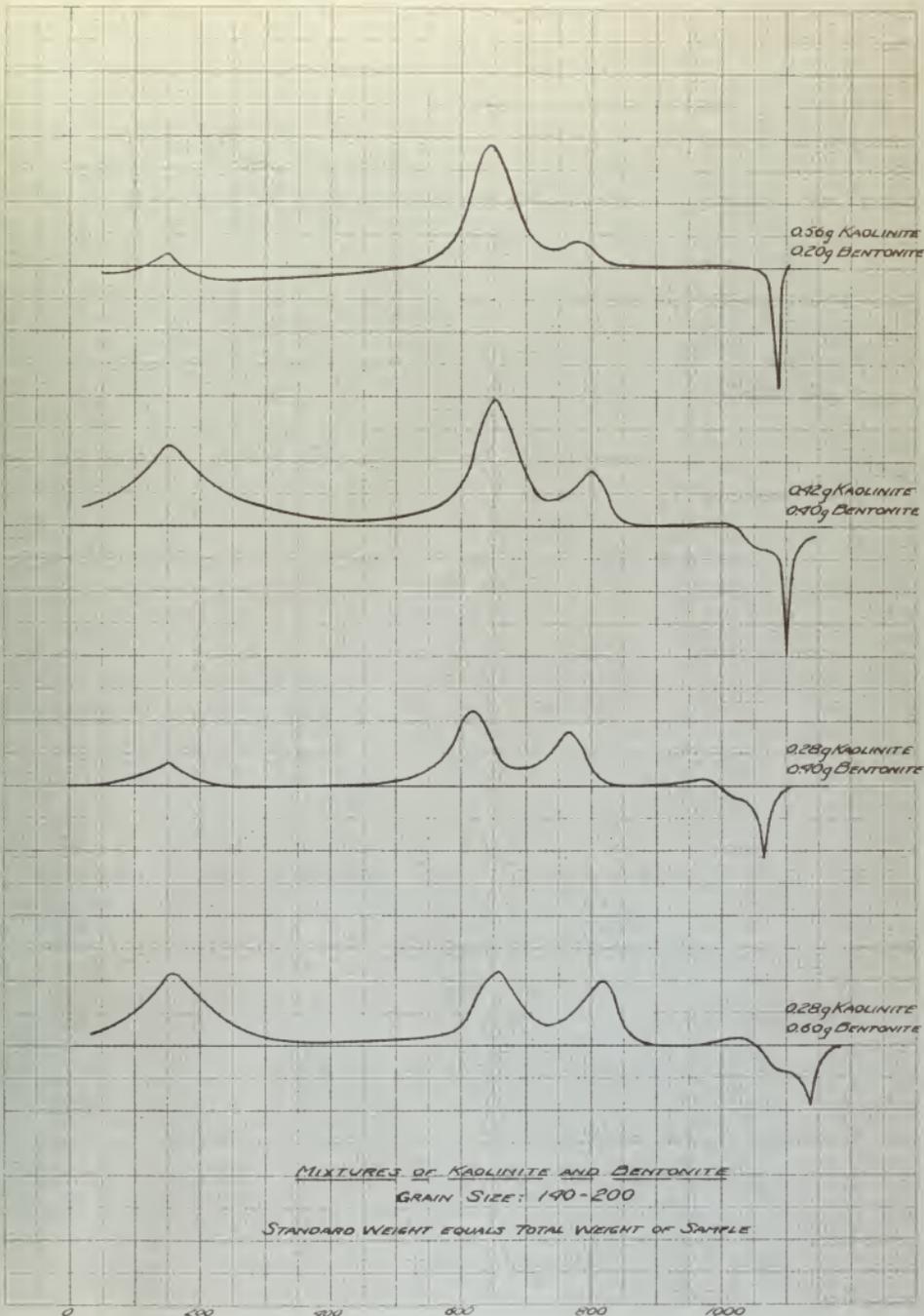
DIFFERENTIAL THERMAL CURVES OF MIXTURES OF KAOLINITE AND BENTONITE

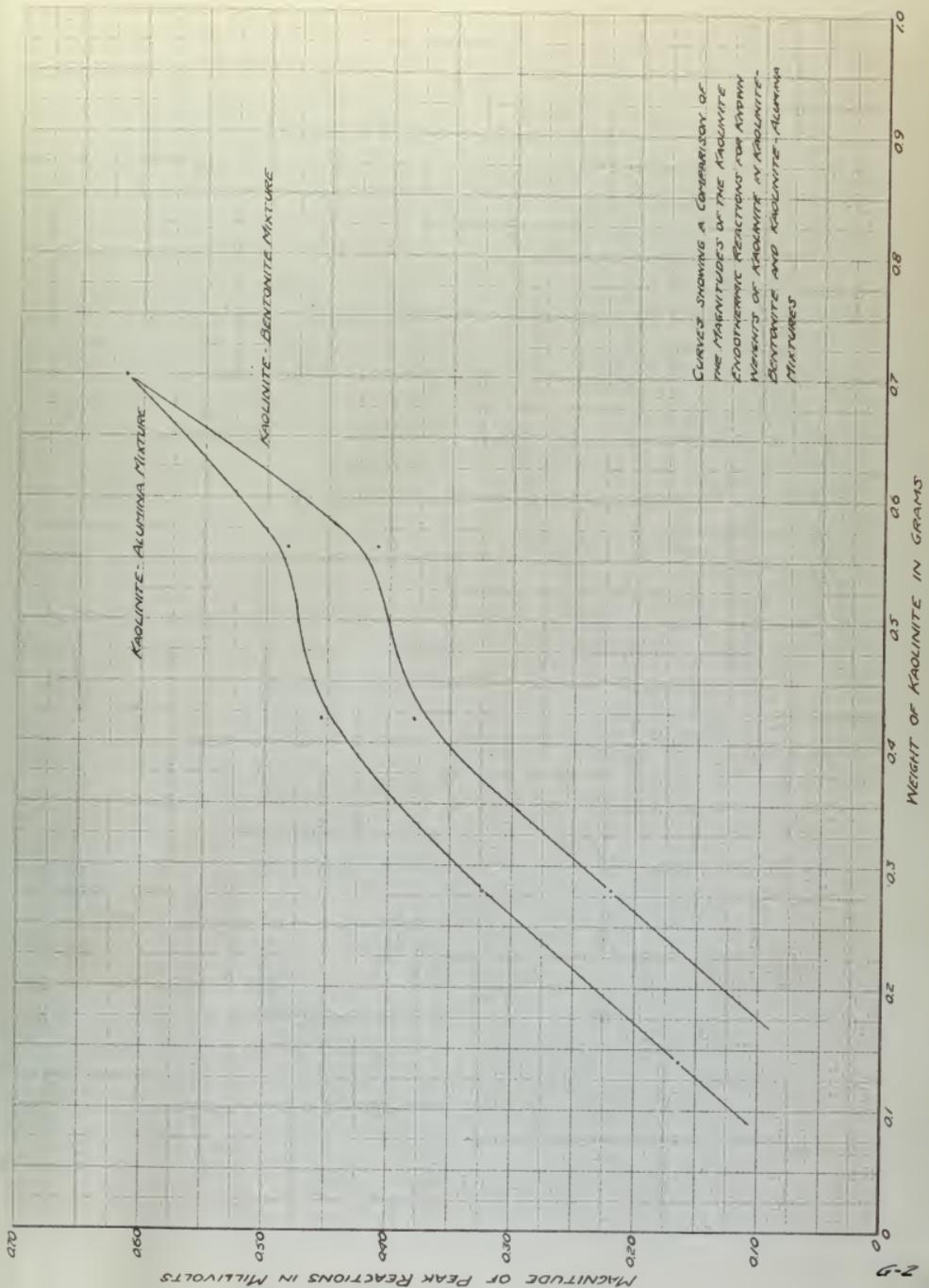
1. Differential Thermal Curves
2. Comparison of Kaolinite Endothermic Reactions
3. Comparison of Bentonite Endothermic Reactions
4. Comparison of Kaolinite Exothermic Reactions.

1910

REPORT OF THE COMMISSIONER OF THE GENERAL LAND OFFICE
FOR THE YEAR 1910

1. THE LAND OFFICE
2. THE LAND OFFICE
3. THE LAND OFFICE
4. THE LAND OFFICE





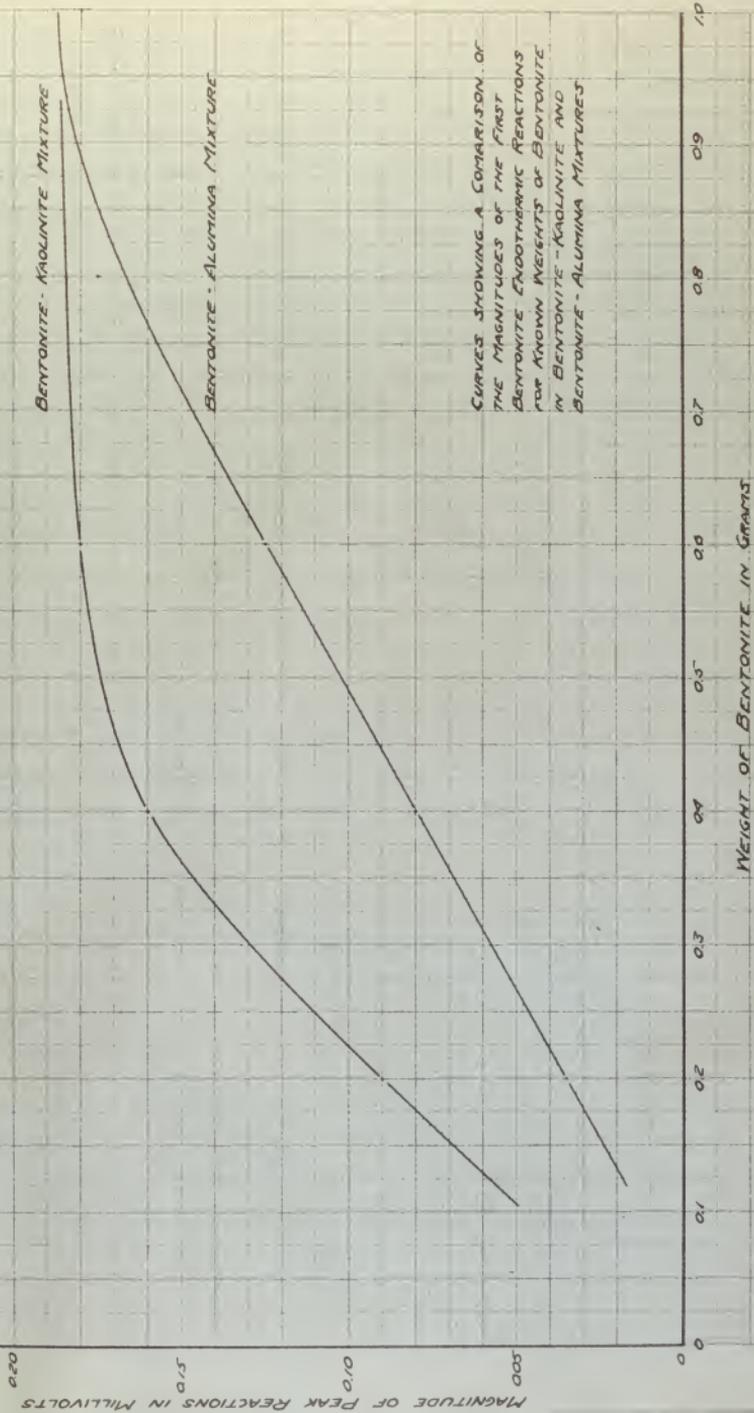
KaOLINITE-ALUMINA MIXTURE

KaOLINITE-BENTONITE MIXTURE

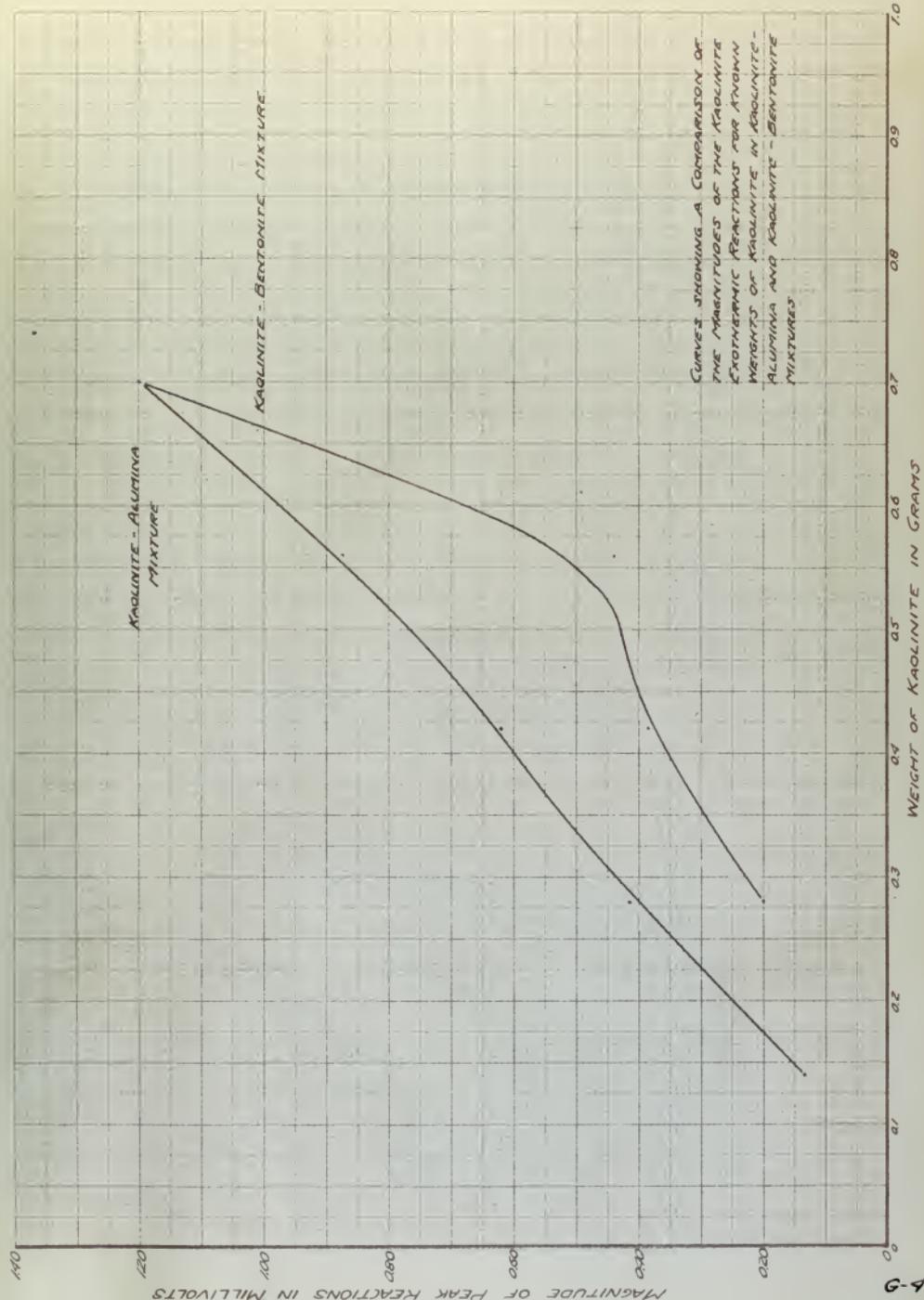
CURVES SHOWING A COMPARISON OF THE MAGNITUDES OF THE KAOLINITE EXOTHERMIC REACTIONS FOR SEVEN WEIGHTS OF KAOLINITE IN KAOLINITE-BENTONITE AND KAOLINITE-ALUMINA MIXTURES

MAGNITUDE OF PEAK REACTIONS IN MILLIVOLTS

WEIGHT OF KAOLINITE IN GRAMS



CURVES SHOWING A COMPARISON OF THE MAGNITUDES OF THE FIRST BENTONITE ENDOTHERMIC REACTIONS FOR KNOWN WEIGHTS OF BENTONITE IN BENTONITE - KAOLINITE AND BENTONITE - ALUMINA MIXTURES



CURVES SHOWING A COMPARISON OF THE MAGNITUDES OF THE KAOLINITE EXOTHERMIC REACTIONS FOR ATOMIC WEIGHTS OF KAOLINITE IN KAOLINITE-ALUMINA AND KAOLINITE-BENTONITE MIXTURES

APPENDIX H

DISCUSSION OF 1750-WATT FURNACE

DISCUSSION OF 1750 WATT FURNACE

The furnace used at the start of this investigation contained a 1000-watt heating element supplied by a one-kilowatt transformer. Although the temperature control mechanism was set for a heating rate of 1023° C per hour, an actual heating rate - as recorded by the Brown Potentiometer - of about 900° C per hour was all that could be obtained. This temperature lag also resulted in a non-uniform heating rate.

It was believed that by replacing the 1000-watt element with a 1750-watt element supplied by a two-kilowatt transformer, the above mentioned difficulties could be eliminated. Two 1750-watt furnaces were ordered from the Hoskin's Manufacturing Company and were installed.

Calibration checks, using alumina in both cells of the sample holders, revealed that an improved heating rate could be obtained but that an extremely erratic differential temperature curve resulted. The difficulty could not be attributed to faulty differential thermocouples because various differential thermocouples were used, some of which had been previously calibrated in the 1000-watt furnace and had been found to be satisfactory.

Further operation and checks of the remaining 1750-watt furnaces resulted in the gradual elimination of the difficulties experienced in the initial use of this element. It is believed that the problem was due primarily to an inherent characteristic of the heating element which was eliminated by continued use.

Since higher and more uniform heating rates can be obtained by use of the 1750-watt elements, it is recommended that the existing 1000-watt elements in two of the furnaces be replaced by 1750-watt elements. In addition, it is recommended that further tests be conducted to determine the true nature of the induced voltage in order to insure the reliability of data obtained by the use of the higher capacity elements.

DEC 72

20939

Thesis
M54

15638

Merritt

The differential thermal analysis of certain clay minerals

The
M5

of

DEC 72

20939

Library

U. S. Naval Postgraduate School
Monterey, California

thes:M54

The diffenretial thermal analysis of cer



3 2768 001 88627 8

DUDLEY KNOX LIBRARY