A STUDY ON THE DIFFERENTIAL THERMAL ANALYSIS OF CLAYS AND CLAY MINERALS

P. L. ARENS

Dit proefschrift met stellingen van

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De Rector Magnificus der Landbouwhogeschool,
H. J. C. TENDELOO

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A STUDY ON THE DIFFERENTIAL THERMAL ANALYSIS OF CLAYS AND CLAY MINERALS

PROEFSCHRIFT
TER VERKRIJGING VAN DE GRAAD VAN
DOCTOR IN DE LANDBOUWKUNDE, OP
GEZAG VAN DE RECTOR MAGNIFICUS
Dr H. J. C. TENDELOO, HOOGLERAAR IN
DE SCHEIKUNDE, TE VERDEDIGEN TEGEN
DE BEDENKINGEN VAN EEN COMMISSIE
UIT DE SENAAT VAN DE LANDBOUW-
HOGESCHOOL TE WAGENINGEN OP
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IX

De tegenstrijdigheid in opvattingen over de invloed van het stikstofgehalte van het tabaksblad op de brandduur, kan grotendeels worden verklaard uit verschillen in fermentatie.

X

De veelvuldige toepassing van repressieve bestrijdingsmiddelen voor plantenziekten betekent een gevaar voor de ontwikkeling van de plantenhygiëne.

XI

Het tijdelijk onder water zetten van terreinen, die bestemd zijn als zaadbedden voor de tabakscultuur, kan worden beschouwd als een plantenhygiënische maatregel ter verkrijging van bibit vrij van slijmziekte.

XII

Voor de bepaling van het warmtegeleidingsvermogen van grond, verdienen niet-stationnaire methoden de voorkeur boven statische.

XIII

De verklaring van het heterosisverschijnsel door een gunstige genencombinatie is onvolledig.

XIV

De gelegenheid tot het houden van publieke promoties aan de Landbouwhogeschool dient verruimd te worden in verband met het veelzijdig karakter van de landbouwkunde.

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STELLINGEN

I

De dehydratatie van kleimineralen kan beschreven worden als een monomoleculaire reactie.

II

Het vóórkomen van amorphe colloiden in de bodem is onwaarschijnlijk.

III

De Friese knipgronden mogen worden beschreven als verouderde solonetz gronden.

IV

De bruine bandjes in de ondergrond van pleistocene zandgronden zijn veroorzaakt door schifting van ijzerverbindingen.

V

De methyleerbaarheid van montmorilloniet is geen bewijs voor de juistheid van de opvattingen van EDELMAN en FAVEJEE omtrent de kristalstructuur van dat kleimineraal.

VI

Bij het verbeteren van de plantenproductie op K-fixerende gronden zijn structuurverbetering en plaatselijke bemesting de aangewezen maatregelen.

VII

De toevoeging van jodium aan leidingwater, ter bestrijding van struma, betekent niet het meest efficient gebruik van deze stof.

VIII

Het is onjuist de waterhuishouding van bodemprofielen te beschouwen los van het microtopografisch verband waarin die profielen voorkomen.

VOORWOORD (PREFACE)

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CHAPTER I

THE DEVELOPMENT OF DIFFERENTIAL THERMAL ANALYSIS AS A METHOD FOR CLAY MINERAL IDENTIFICATION

§ 1. Introduction.

The heating of clay minerals causes more or less discontinuous changes in their composition and constitution. These changes are accompanied by certain heat effects. Thus loss of water and loss of CO_2 invariably are endothermic reactions. By means of the differential thermal analysis (DTA) these heat effects may be recorded in a convenient way as a function of temperature. Thereto a certain amount of clay, contained in a sample holder, is heated in a furnace from room temperature to about 1000°C or even higher. At the same time a thermally inert comparison substance is heated under the same conditions. The furnace temperature is measured by means of a thermocouple, usually mounted in the inert substance, while the reactions in the clay sample are measured by means of a differential thermocouple. One junction of the differential thermocouple is mounted in the clay sample and the other junction mounted in the inert substance. The differential thermocouple arrangement was first developed by WALLACH (see 280) *). In temperature ranges where no reaction occurs in the clay, the temperature difference between the clay sample and the inert sample is zero, and the e.m.f. of the differential thermocouple is zero. An endothermic reaction in the clay causes a lag in temperature of the clay sample behind the temperature of the inert substance. The resulting temperature difference is recorded by the differential thermocouple. For exothermic reactions the e.m.f. of the differential thermocouple is in the opposite direction to that for endothermic reactions. Thus reactions in the clay sample, accompanied by any heat effects, whatsoever, may be followed as a function of the temperature of the inert substance. In fig. 1 a schematic representation is given of a DTA-curve of montmorillonite, showing the reaction temperature range, the intensity of the reaction and the recorded sign of the heat of reaction.

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*) The figures in parentheses refer to literature cited, p. 107

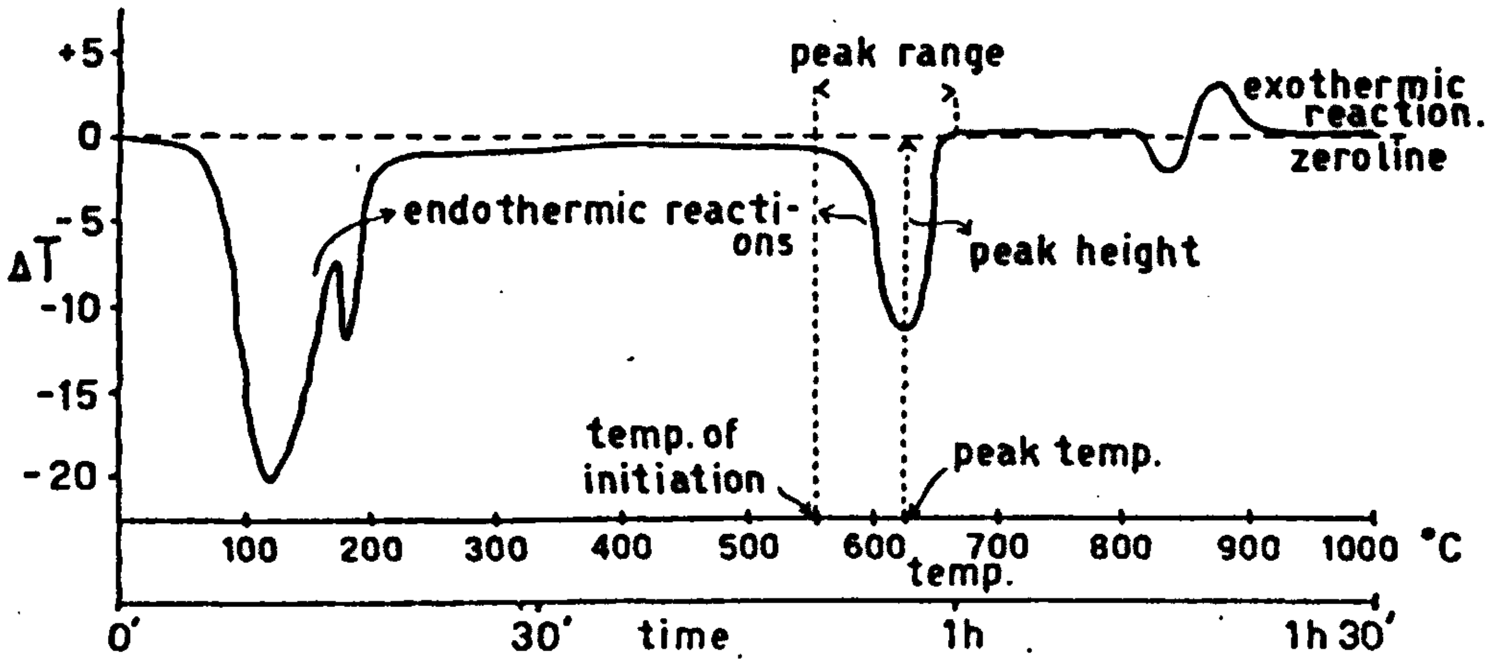

fig. 1. Schematic representation of a DTA curve of Ca-montmorillonite, showing endothermal and exothermal reactions, peak temperature, peak range and peak height.

The reaction ranges, the intensity of the reactions and the sign of the heat of reaction, are typical for the different clay minerals, thus enabling their distinction and identification.

§ 2. Historical.

LE CHATELIER (54) was the first to apply thermal analysis to clays. As early as 1887 he distinguished five different clay species, with regard to their thermal behaviour, viz. halloysites, allophanes, kaolinites, pyrophillites and montmorillonites.

The method, later improved by WALLACH and then called the differential thermal analysis, remained unknown for a long time. The first workers, who used the DTA after LE CHATELIER were the ceramists (86, 147, 273, 284) and pure mineralogists (225-227, 179), while applications to pedology, to agricultural soils and clay separates, were first made in 1935 by AGAFONOFF and JOURAVSKY (1, 2). After 1935 the importance of clay mineral research became widely recognized and the method rapidly popularized all over the world. The main advantage of DTA over X-ray analysis, lay in the fact that the equipment used for DTA is relatively simple, so that even the smallest laboratories could be equipped with it. For descriptions of the equipment see: 21, 24, 26, 39, 46, 91, 104, 107, 116, 135, 141, 152, 158, 174, 177, 219, 226, 228, 253, 254, 271, 276.

In the course of the years many improvements of the technique have been proposed. These improvements were mainly concerned with the recording and controlling equipment. LE CHATELIER and SALADIN (see 41) described the use of a prism of Lissajous to connect the lightbeams of the two recording galvanometers to one beam. The movement of the light beam from one mirror occurs in a horizontal plane, from the other, in a vertical plane. After passage through the Lissajous prism the horizontal movement of the light spot describes the temperature rise of the furnace and the vertical movement describes the temperature difference between clay and inert substance. This prism device is still used in several French and Belgian laboratories (CAILLERE and HENIN, MUNIER, WAEGEMANS, etc.). The main improvement to the technique seems the use of electronic equipment, a.o. described by KERR and KULP (174), for controlling and recording purposes. As will appear from chapter 4, the rate of temperature rise of the furnace is of outstanding importance for the result. So a constant heating rate, expressed as °C per unit of time, may considerably simplify the interpretation of the recordings. There are various other ways to obtain a constant heating rate (e.g. the use of variable resistances or of variable transformers) but electronic controlling equipment probably is the best. The use of an amplifier for an improved record of the differential temperature is described by BECK (21). HENDRICKS and coworkers (141) described a portable DTA equipment, for use in field stations.

Due to the fact that many factors, involved in determining the general shape of DTA curves, were underestimated or unknown, there appeared many controversial papers as to the applicability of the method. A number of investigators (148, 187, 237) rejected the method, but most of the others persisted in the use of it. It is the objective of the present study to point out the factors, which are important in determining the shape of the curves.

§ 3. Qualitative interpretations.

For qualitative purposes (identification) the method has proved to be useful due to the work of CAILLERE and HENIN (41), HENDRICKS and ALEXANDER (135), NORTON (219), GRIM and coworkers (104, 105), KELLEY (166), SPEIL and coworkers (271), GORBUNOV (94) and others.

The following measurable items are of interest in the qualitative interpretation of recordings (for explanation see fig. 1):

a. the general shape of the curve, determined by the nature of the clay under consideration;

b. the temperature range of the reactions, as measured from the initiation (departure from the zero-line) to the end (return to the zero-line);

c. the temperature at the maximum rate of reaction (peak temperature);

d. the intensity of the reactions, measured, for the time being, as the peak-height.

These quantities differ for the different clays, even within the same clay-mineral group.

The best described thermal reactions are those accompanied by loss of material, as for instance dehydration reactions. These reactions were already known from early thermal analysis records, where the loss-in-weight upon heating was plotted against temperature. Especially the dehydration reaction of kaolinite, which is known to occur from about 430°C to 650°C has received considerable attention (237), because of its industrial importance.

The kaolinite minerals, the halloysites and the hydrous oxydes of Al and Fe give the most easily distinguishable results with DTA. The reactions exhibited by these minerals upon heating are of fairly strong intensity, and limited to a well defined temperature range. The minerals of the montmorillonite group and, still more, the illite minerals usually yield curves with reactions of relative low intensity, the reactions being variable over a wide temperature range. This behaviour probably is caused by the variable chemical composition of the latter minerals. The first fairly good DTA curves of illites were given by GRIM and his coworkers (100, 105). The vermiculites are also rather variable with regard to thermal decomposition. The carbonates on the other hand yield pronounced curves, exhibiting reactions of strong intensity. In chapter 6, table the reaction ranges and the reaction intensities for the different minerals occuring in the clay fraction of soils are summarized.

A comparison of DTA curves with dehydration curves, obtained by plotting weight-loss upon heating against temperature reveals that the results may diverge considerably. The DTA curves show the reaction ranges and the maxima of the reactions at higher temperature, than do dehydration curves. The difference is probably one which may be expected upon comparing a dynamic (continues) process (DTA) with a static (discontinues) process (stepwise dehydration). In chapter 4 the implications of this statement will be developed further.

Comparison of curves of one and the same sample of clay, submitted to DTA in different equipments, as has been carried out by DE LEENHEER (187) and MACKENZIE (191), indicated that DTA curves may have no general validity. The differences of reaction temperatures from the same sample of clay amounted to 150°C or more, when curves resulting from different equipments were compared. The present author has indicated (12) that the cause of the discrepancies is to be sought for primarily in the nature of the furnace and the temperature recording and controlling equipment. It is to be expected that the difficulties in the interpretation of curves will increase as do the number of different kinds of equipment.

Some of the interpretative difficulties have already been clarified by HOULDSWORTH and COBB (147), PIETERS (237) and JEFFRIES (158). The former authors emphasized the importance of the rate of temperature rise of the furnace upon the thermal curves of kaolinites. The steeper were the heating rates, the more did the measured reaction temperatures diverge from the true reaction temperatures known from static measurements. The phenomenon of displacement of reaction temperatures is called peak-shifting. PIETERS has pointed out that there is an influence of the partial vapour pressure of water in the reaction medium upon the temperature of dehydration of kaolinite. High partial vapour pressures of water may cause a delay of this reaction amounting to 170°C. From JEFFRIES work it follows that the heat capacities of the clay sample and the inert sample should be equal, if one is to obtain straight zero-lines for the temperature ranges where no reaction occurs.

For reactions not accompanied by any loss of material the comparability of DTA curves is much better. Examples of such reactions are the conversion of α-quartz into β-quartz at 573°C, the exothermic reaction of kaolinite at about 950°C and the conversion $\gamma\text{-Fe}_2\text{O}_3 \rightarrow \alpha\text{-Fe}_2\text{C}_3$ at about 510°C. The reaction temperatures in these cases are fairly well defined; the intensity of the reactions, however, may be modified considerably, as will be shown in chapter 3.

In table 1 a number of references is given referring to the literature on qualitative interpretation of DTA curves from the various clay minerals indicated.

TABLE 1.

Reference table to the literature on qualitative interpretation of DTA-curves from various minerals present in soils and clays.
The numbers refer to lit. cit., pag. 107.

Group	Minerals	References
Oxides and hydrous oxides	Al-hydroxides	3, 8, 21, 24, 26, 46, 54, 94, 105 123, 166, 174, 179, 218, 219, 220 226, 270, 271.
	Fe-hydroxides	3, 21, 24, 26, 52, 105, 166, 174, 259, 270.
	Quartz	21, 24, 25, 26, 78, 86, 105, 109, 123, 166, 174, 177, 270.
	Mn-oxides	232.
Kaolinitegroup	Kaolinite	1, 3, 4, 7, 8, 21, 24, 26, 41, 46, 54, 60, 64, 91, 94, 99, 101, 104, 105, 107, 116, 117, 123, 135, 147, 152, 158, 166, 174, 177, 179, 187, 219, 220, 226, 227, 251, 254, 270, 271, 275, 284.
	Fire-clay-min.	60, 91, 104, 105, 107, 174, 220, 270, 271.
	Dickite	21, 94, 152, 174, 270, 271.
	Anauxite	21, 152, 174.
	Nacrite	174.
	Halloysite	21, 24, 26, 41, 45, 46, 54, 64, 91, 94, 105, 123, 158, 166, 174, 179, 219, 270, 271.
Montmorillonite group	Montmorillonite	1, 3, 4, 7, 21, 24, 26, 39, 41, 43, 46, 54, 60, 91, 94, 99, 100, 101, 104, 105, 116, 123, 135, 139, 158, 166, 174, 177, 179, 219, 226, 227, 228, 236, 251, 254, 262, 270, 271.
	Beidellite	3, 24, 46, 166, 174, 219, 228, 251, 271.
	Nontronite	9, 45, 46, 90, 174, 177, 185, 226.
	Hectorite	5, 45, 166, 174, 177, 228.
	Saponite	21, 94, 174, 228.

T A B L E 1. (continued)

Group	Minerals	References
	Attapulgite	44, 45, 46, 158, 174, 270.
Mica group	Illite	3, 7, 9, 15, 21, 24, 26, 39, 41, 46, 59, 60, 91, 94, 99, 100, 101, 104, 105, 135, 158, 166, 174, 179, 219, 251, 254, 270, 271.
	Vermiculite	15, 16, 57, 146[a], 278.
	Chlorites	3, 5, 46, 50, 225.
	Antigorite	47, 48, 225.
	Pyrophillite	45, 54, 123, 179.
Carbonates	Calcite	22, 24, 26, 46, 61, 77, 79, 80, 105, 174.
	Magnesite	22, 24, 26, 46, 61, 77, 105, 174.
	Dolomite	22, 24, 26, 46, 61, 77, 105, 174.
	Aragonite	79, 80.
	Siderite	21, 22, 61, 89, 173, 249.
	Other carbonates	22, 61, 174, 178.
Phosphates	Various	197.
Clay-organic matter complexes		2, 9, 31.

But is must, however, be emphasized that correct qualitative interpretation of thermal curves is impossible without knowledge of the factors underlying the lags in reactions. The way in which these factors may be evaluated will be considered in chapter 4.

Finally it may be stated that nowadays the opinion prevails (191) that DTA curves obtained with one and the same equipment, operating under strictly reproducable conditions, are comparable among themselves, so long as operating conditions are kept constant. The generalization of results among different equipments which do not operate under identical conditions is still a matter of considerable difficulties. In other words: the method is strictly conventional (12).

Nevertheless it will be shown in chapter V how the generalization of results may be approximated.

§ 4. Quantitative interpretation.

The first quantitative interpretations of DTA curves were made by AGAFONOFF (1). Visual comparison of curves, drawn from artificially prepared mixtures of clay minerals, with curves from N.-African clays, gave an impression of the relative quantities present in the latter. NORTON (219) suggested, that the magnitude of the galvanometer deflection accompanying a thermal reaction (measured as the height of the peak), would be proportional to the quantity of the mineral present. This same view is held by GRIMSHAW and coworkers (108). Several other investigators, as ALEXANDER, HENDRICKS and NELSON (7), SCHAFER and RUSSELL (254), SPEIL and coworkers (271), KERR and KULP (174) have considered the area under the reaction peaks to be proportional to the concentration of the mineral under consideration. The former authors (7) derived the relation empirically, the latter (174) both empirically and theoretically. The observations made by DEAN (64) however are in disagreement with the supposition that the area under the peak is proportional to the concentration of reacting material. DEAN considers the cosecant of the peak angle as a quantitative measure, though his material is restricted to the clay minerals showing pronounced endothermic reactions.

JEFFRIES (158) attacked the problem from a totally different view point, putting the heat capacity of the clay sample before and after a reaction as a measure of the relative quantities present.

From the available data, it is possible to derive certain empirical relations, with the restriction that these relations only hold for the operating conditions of the equipment under consideration.

It seems however doubtful, whether a correct understanding of quantitative DTA is possible without complete knowledge of the kinetics of the reactions. The derivation of a general relation between reaction-curve and the concentration of the reacting claymineral involves an understanding of

a. the kinetics of the reaction;
b. the heat-balance of the furnace, including the sample holder the clay and inert material and the heat supply to the reactant.

The kinetics of reactions of the type

$$AB_{solid} \rightarrow A_{solid} + B\uparrow_{gas}$$

are rather obscure. The best known reactions of this type are the decomposition reactions of the carbonates (150, 286). Of the silicate minerals the kinetics of the dehydration of kaolinite has been the subject of a number of investigations. The early work is summarized by PIETERS (237). Of the later work that of MURRAY and WHITE (214) is of outstanding importance. Its bearing upon quantitative DTA will be discussed later.

About the rôle played by the movement of heat in the clay sample during a reaction, little is known until now, though its influence may be assumed substantial in view of quantitative thermal analysis (chapter 4).

§ 5. The purpose of this study.

From the foregoing discussion of the literature it appears that several basic quastions related to the (qualitative and quantitative) explanation of DTA curves are still unsolved, though the method is the eldest applied to clay research.

It is apparent that a number of factors, residing in the DTA apparatus, are to a great extent rate determining for the observed reactions. The first question is: what are these apparatus-bound factors and what is the relative importance of each of these upon the recorded result. In order to solve this question various furnaces, sample holders, thermocouples and sensitivity scales have been used in this study, while from a number of foreign laboratories analyses from the same sample of clay were obtained, with knowledge of their operating conditions. It will be shown in chapter IV and V how these apparatus-bound factors may be adjusted, in order to generalize the results, and how these factors may be used to modify the recorded curves.

Besides the influences, resident in the equipment, there are properties, of the clay alone, which determine the course of DTA curves. The second problem is to reveal these latter factors, (particle size, cations adsorbed, degree of crystallization, etc.) and their relative influence on the recorded results.

If an answer is found to these two questions, the qualitative interpretation of DTA curves is considerably simplified, and the phenomenon of peak shifting, which is the crux of thermal analysis, might also be understood. There remains however the question whether there is any observable difference between the reactions, which are accompanied by loss of material, and the reactions, which are not accompanied by any loss of material. The answer to this question would enable one to correlate the loss-in-weight upon heating data and dilatometer data with DTA.

Finally the question of quantitative DTA rises, but this question may not be solved without knowledge of the first three. Here the problem is to find a relation between the quantity of a clay component and the rate of reaction in a non-static reaction process, the rate determining factors and the time of reaction being known. This is a matter of considerable difficulty and will be the subject of part of chapter 4.

With the answers to the foregoing question known, one can write down the items involved in an eventual standardisation - if wanted - of the DTA equipment. DTA standardisation will be the subject of appendix 2.

CHAPTER II

DESCRIPTION OF THE EQUIPMENT AND OF THE MATERIALS USED FOR TESTING

The equipment, needed for DTA consists of:

1. a furnace, ranging from room temperature to about 1000°C;
2. equipment controlling the temperature rise of the furnace;
3. a sample holder with room for clay sample and inert sample mounted in the furnace;
4. equipment for recording the temperature of the furnace and for recording the difference in temperature between the clay and the inert sample.

The whole is arranged as is shown schematically in fig. 2. Many modifications of this arrangement are in use (BECK, BERKELHAMER, BERKELHAMER and SPEIL, CAILLERE and HENIN, GRIM and ROWLAND, GRIMSHAW, HEATON and ROBERTS, GRUVER, HENDRICKS and ALEXANDER, HENDRICKS, GOLDRICH and NELSON, JEFFRIES, KERR and KULP, KULP and KERR, MUNIER, NORTON, SCHAFER and RUSSELL, SPEIL BERKELHAMER, PASK and DAVIES, and others).

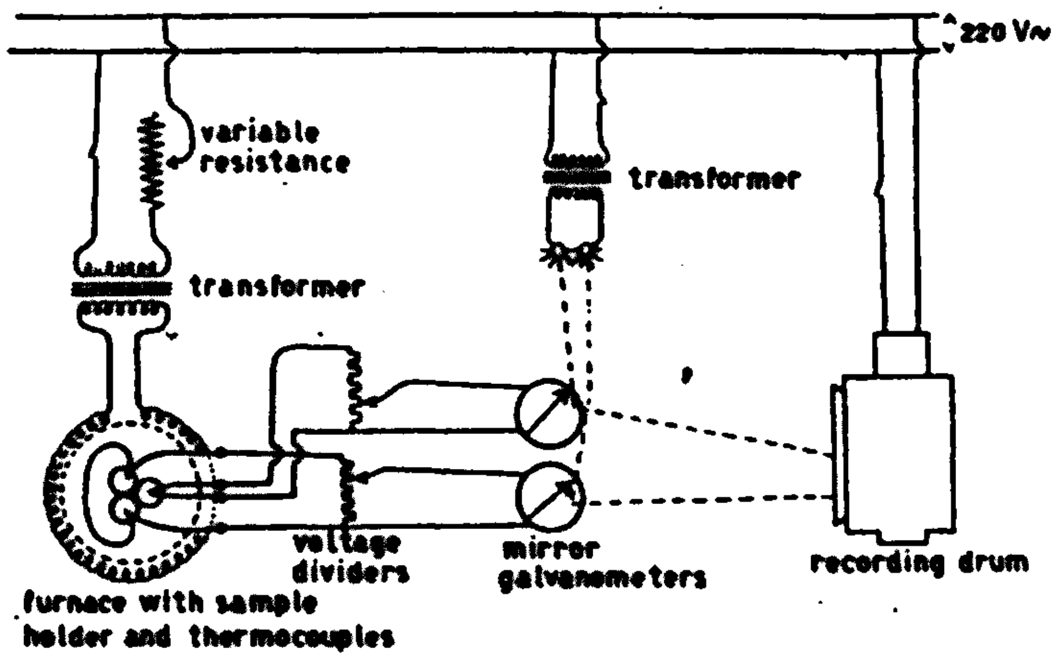

fig. 2

The furnace and the equipment controlling the temperature rise.

In this study three types of furnaces have been used, designated as No. I, II and III. This was done in order to reveal any influence of the nature of the furnace.

Furnace No. I is a commercial Gallenkamp furnace, operating on 220 volts a.c., with internal resistance of 21 ohms at room temperature and 26 ohms at 1000 degrees C. The door of this furnace was removed and replaced by a slide constructed of high duty silica brick and mounted with a horizontal alundum platform in the middle, upon which the sample holder could be placed. The sample holder was filled outside the furnace, and afterwards placed on the platform. After the placement of the thermocouples in the clay sample and in the inert substance, the slide was introduced in the furnace. The arrangement of furnace, slide, sample holder and thermocouples is shown in fig. 3.

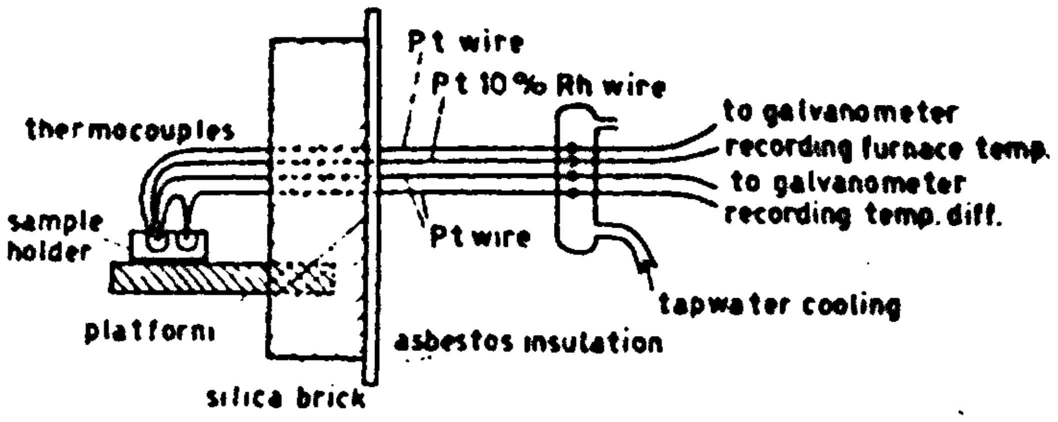

fig. 3

The rate of heating of this furnace was manually controlled by a variable resistance ranging from 40 to 0 ohms, thus enabling a temperature rise of about 8 degrees C per minute (see fig. 6).

Furnace No. II is a home-designed DTA-furnace, the diameters of which are given in fig. 4 *). This furnace had the main advantage that the active space was small, and that heating took place from all sides, enabling a very regular temperature rise. The total internal resistance was 2.2 ohms at room temperature and 2.4 ohms at 1000°C, the heating element being Kanthal-A wire, diameter 1.8 mm. This furnace operated maximally under 40 volts a.c., delivered via a transformer 380 V / 40 V. In the primary current of the transformer a variable resistance (60 - 0 ohms) was placed, enabling a temperature rise of about 13.5 degrees per minute (see fig. 6).

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*) The refractory bricks were produced by N.V.Chamotte Unie, Geldermalsen. We are indebted to Ir G. van Gijn and H. van Dijk for their assistance in the design of the furnace.

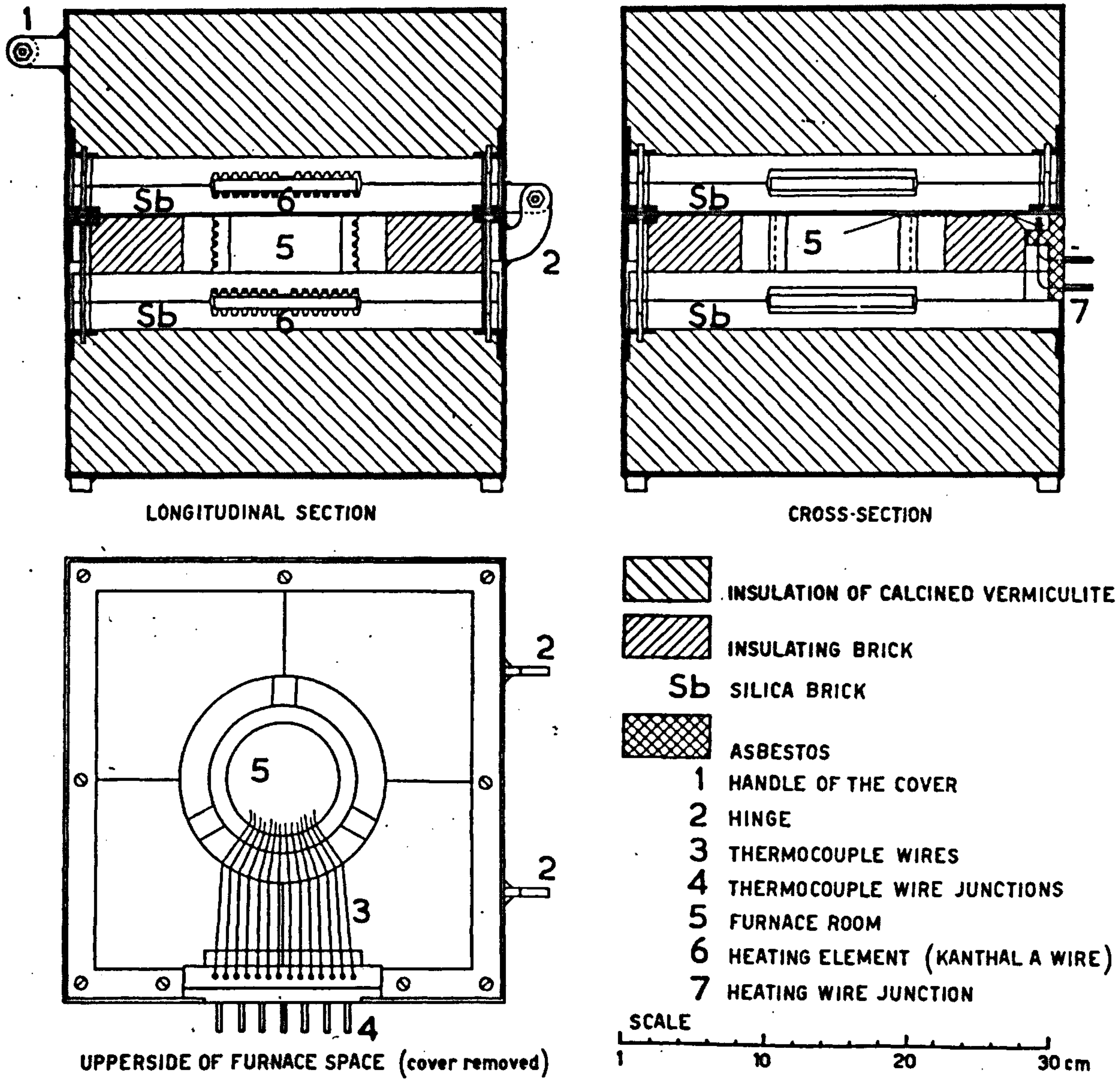

FIG. 4

Furnace no.II, designed by
N.V. Chamotte Unie Geldermalsen.

Most of the experiments, mentioned below, were carried out with this furnace.

Furnace No. III is a commercial Heraeus tube furnace operating on 127 volts a.c. with internal resistance of 35 ohms. The internal diameter of the tube was 3 cm, the length of the tube 18 cm. This furnace was hung, with vertical tube, between two pulleys and could be removed by means of two contra-weights to which it was attached with steel wire. In experiments with this furnace, the sample holder was fixed on a vertical alundum tube which just fitted into the lower end of the furnace tube. The arrangement of furnace, sample holder and thermocouples is shown in fig. 5.

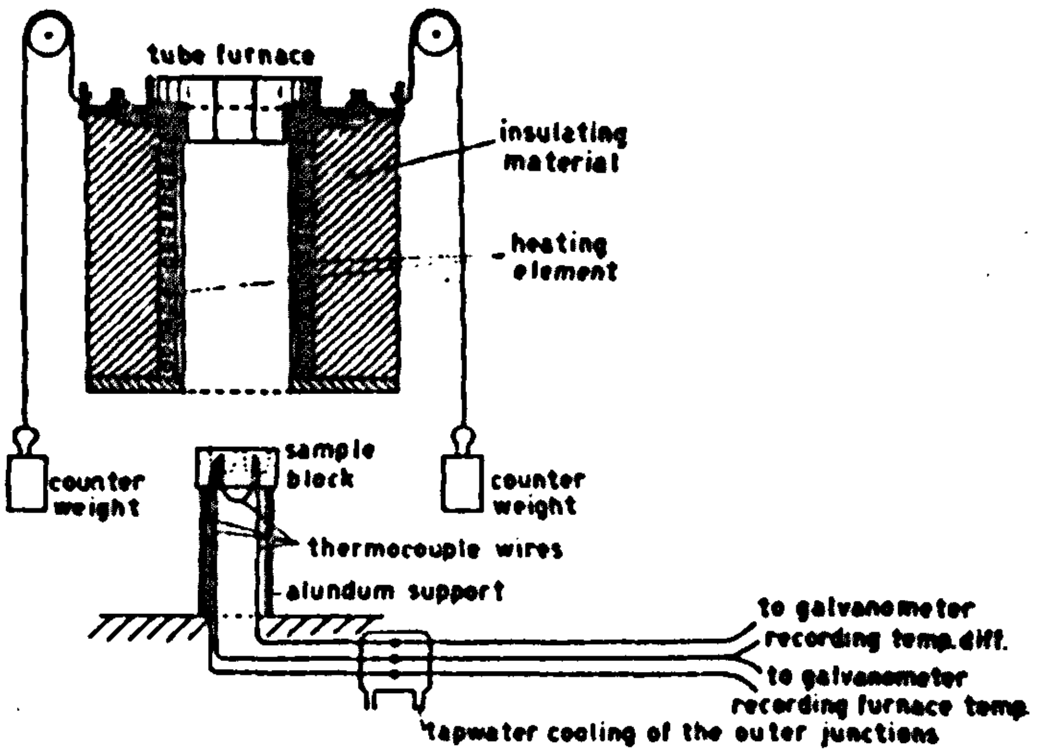

fig. 5

The heating rate of this furnace was accurately linear from 80 to 700°C. By means of a variable resistance ranging from 44 to 0 ohms in the furnace current circuit the heating rate could be regulated and amounted to approximately 28 degrees C per minute (see fig. 6).

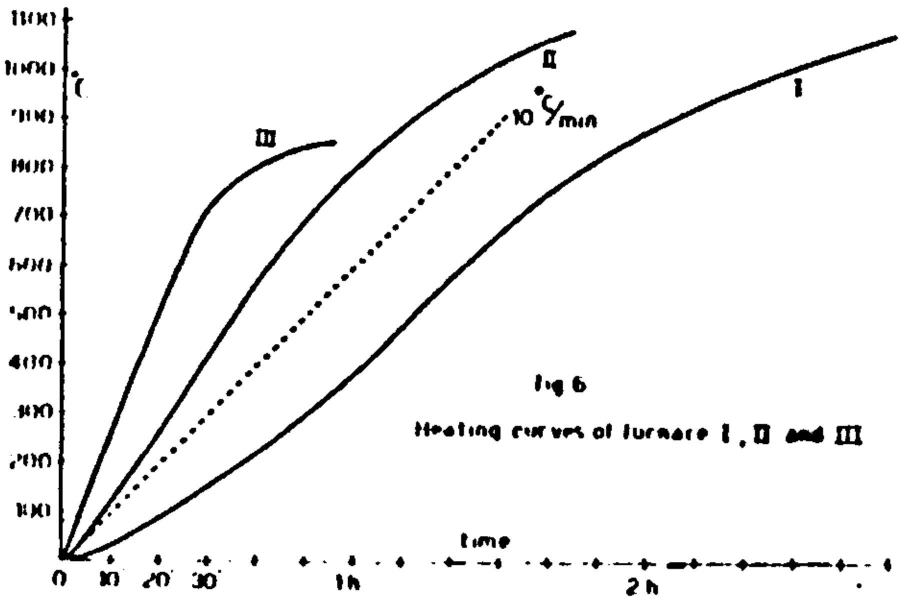

fig. 6

In general it may be stated, that a great variety of furnaces is adaptable to DTA, but those having an approximate linear temperature rise over the whole temperature range should be preferred. Adequate insulation is very important; the better the insulation is, the less it appears to be necessary to watch over the regulation of temperature rise.

Further the furnace should answer the following conditions: low heat capacity of the active furnace space, for rapid response of furnace temperature to variations in heat input; high coefficient of heat transfer to the sample holder; good sized heating elements arranged in such a way that heat gradients in the furnace-room are minimized; and adequate closing to prevent air currents from disturbing the heating process.

In this study no use has been made of electronic controlling equipment for accurately linear furnace temperature rise. It has been the primary objective to survey the suitability of DTA as a method of identification for clay minerals under divergent experimental conditions.

The sample-holders.

In the literature various types of sampleholders have been described. CAILLERE and HENIN work with quartz-glass tubes. Most Brittish workers prefer ceramic sample-holders: MACKENZIE, ROBERTS and GRIMSHAW; MUNIER in Sèvres; LEPINGLE in Brussels; and WAEGEMANS in Tervueren. In the U.S.A., however, sampleholders with high heat-conductivity coefficients are preferred (nickel, inconel, platinum etc.). See the work of NORTON, HENDRICKS and ALEXANDER, GRIM and coworkers; SPEIL and coworkers; KULP and KERR, GRUVER, etc.

To cover the influence of the sample holder on the initiation and the course of the reaction, various types of containers have been compared. The following were used (see fig. 7):

Nickel sample-holders.

a. cylindrical block, diameter 45 mm, height 18 mm, with two holes, diameter 10 mm, depth 15 mm;

b. rectangular block, 40 x 40 x 15 mm, with two holes, diameter 5 mm, depth 9 mm;

c. rectangular block, 36 x 36 x 8 mm, with two holes, diameter 6 mm, depth 6 mm;

d. rectangular block, 48 x 48 x 16 mm, with two holes, diameter 8 mm, depth 12 mm and two holes oppositely located, diameter 4 mm, depth 8 mm;

e. rectangular block, 22 x 8 x 15 mm, with three holes, diameter 6 mm, depth 12 mm.

Ceramic sample holders:

f. alundum tubes, external diameter 10 mm, internal diameter 7 mm, depth 15 mm;

g. alundum tubes, external diameter 5 mm, internal diameter 3 mm, depth 12 mm;

h. cylindrical block, diameter 48 mm, height 16 mm, with two holes, diameter 11 mm, depth 12 mm;

j. cylindrical block, with diameter as h, but with two holes, diameter 8 mm, depth 12 mm.

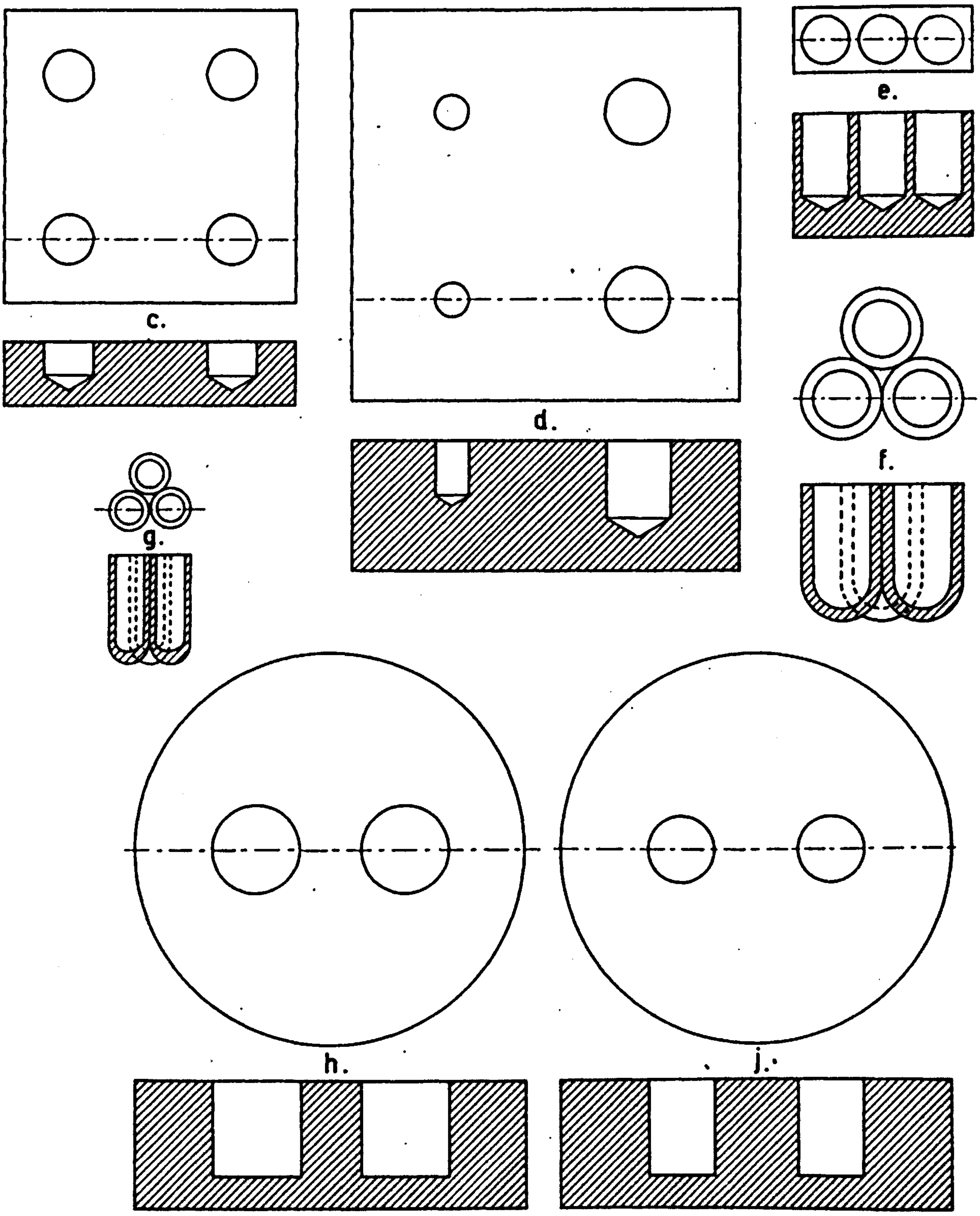

FIG. 7

Cross sections and longitudinal sections of the sample blocks c, d, e, f, g, h and j, used in this study.

Furnace temperature and difference temperature recording equipment.

All temperatures were measured by means of Pt - Pt 10% Rh thermocouples. To study the influence of wire diameter two different sets of thermocouples were used, respectively with wire diameter 0.2 mm and 0.5 mm.

In most experiments the furnace temperature junction was placed in the clay sample, though a number of experiments were made with the hot junction placed in the inert substance. The corresponding cold junction of this couple was maintained at constant temperature, for which streaming tap water was used. The tapwater temperature differed from 12 degrees C in early autumn (maximum) to 8 degrees C in early spring (minimum) and was measured at regular intervals. The difference of 4 degrees between spring and autumn temperature of the cold junction was left out of consideration in the measurement of the furnace temperature. In most measurements 10 degrees C was maintained as cold junction temperature and consequently the error is ± 2° C, lying within the error of the observation.

The differential thermocouples had both junctions in the furnace, one in the inert substance, the other in the clay. Outside the furnace the Pt wire-ends were attached to copper wires, both junctions with copper being maintained at the same constant temperature in a tapwater cooling device.

The recording equipment consisted of two Moll-Original mirror galvanometers of high sensitivity*). One measured furnace temperature, the other differential temperature, the reflected lightbeams being recorded continually on photographic paper, mounted on a recording drum driven by a synchronous motor.

In both thermocouple circuits voltage dividers were placed to adjust the galvanometer deflections to the given width of the recording paper. The resistance of the galvanometer shunt had a constant value of 675 ohms for aperiodic damping. The e.m.f. of the furnace temperature thermocouple was divided 1 : 100, the result being that one centimeter recorded galvanometer deflection corresponded to 95 degrees C. The e.m.f. from the difference temperature thermocouple was much less divided; various sensitivity scales have been used, depending on the experimental conditions (sample weight, sample holder, velocity of temperature rise, etc.) and on the nature of the clay.

The sensitivity scales varied from 1 cm recorded deflecti-

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*) Kipp en Znn., Delft, Moll-Original galvanometer.

on for 22 degrees C to 1 cm deflection for 0.4 degrees C difference temperature. The time to reach equillibrium-deflection upon a sudden e.m.f. exposure was 1.2 sec. for both galvanometers, see fig. 9.

The recording drum had a circumference of 42 cm and an effective width of 12 cm. Time of rotation was 160 minutes, so that for normal work with furnace No. II two subsequent recordings could be made on one film. The photographic paper used was Gevaert bromide paper of medium sensitivity, supplied with parallel lines on 5 mm distance to facilitate reading of the curves (see fig. 8). After every two runs the paper was removed from the drum, developped in metholhydrochinon 1 : 6, fixed in acid fixative, washed and dried.

Calibration of the thermocouples.

The calibration of the furnace-temperature thermocouple was carried out according to the method of FAUST (78), using the $\alpha \rightarrow \beta$-quartz inversion at 573°C. The observed variability of this inversion is 1,89°C, thus lying within the experimental error in reading the furnace temperature line. The e.m.f. of the Pt - Pt 10% Rh thermocouple at 573°C (cold junction at 9°C) is 4.90 mV. The recorded galvanometer-deflection at 573°C was accurately the same as the recorded deflection of an applied e.m.f. of 4.90 mV.

The differential thermocouple was calibrated empirically with each of the two junctions placed in a waterbath of different temperature, the temperature of which was measured with a precision mercury thermometer. In the graph of fig. 9 the observed magnitude of the galvanometer deflection is plotted against difference temperature.

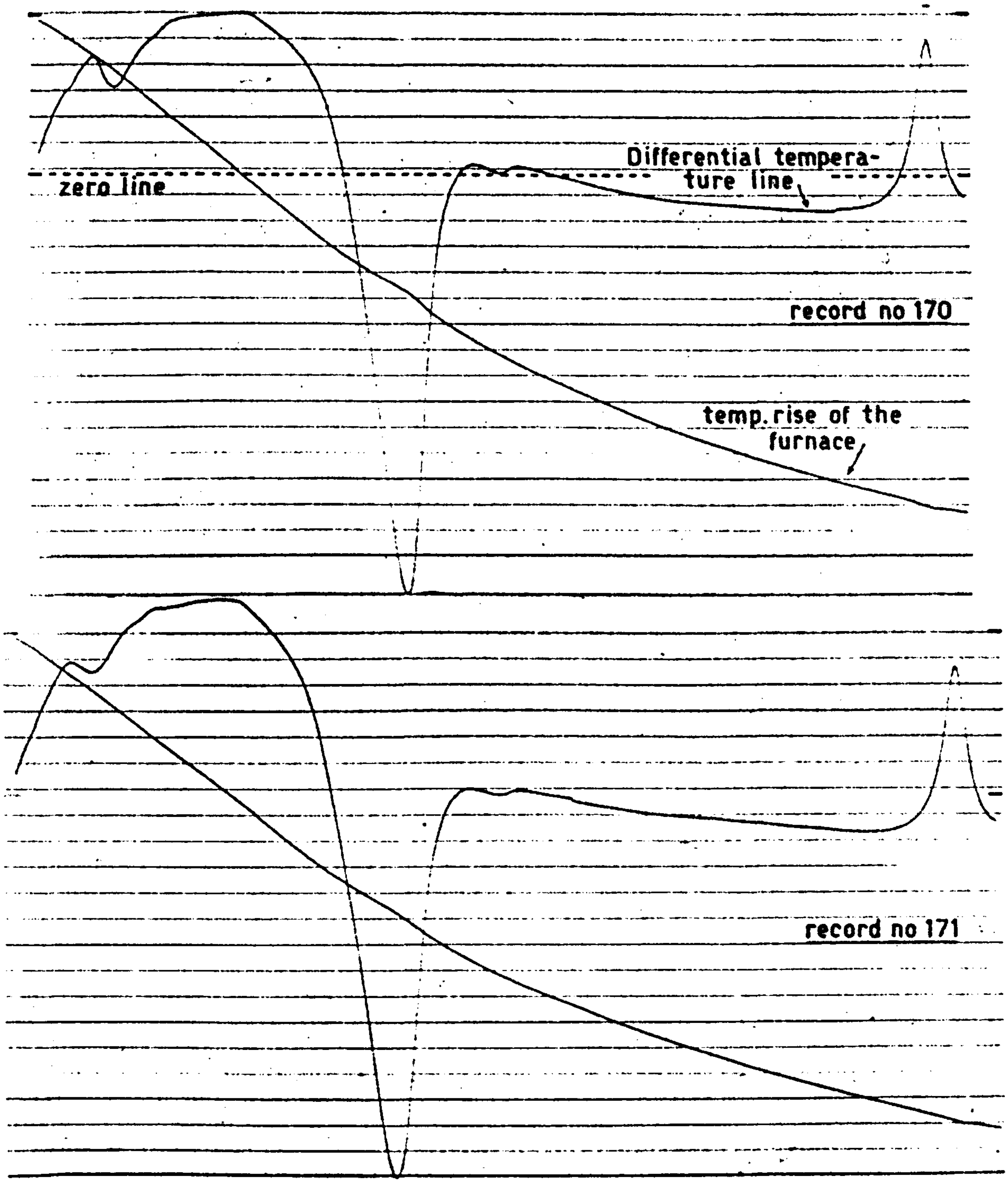


fig. 8. Original duplicate recording of a mixture containing 90% kaolinite and 10% montmorillonite.

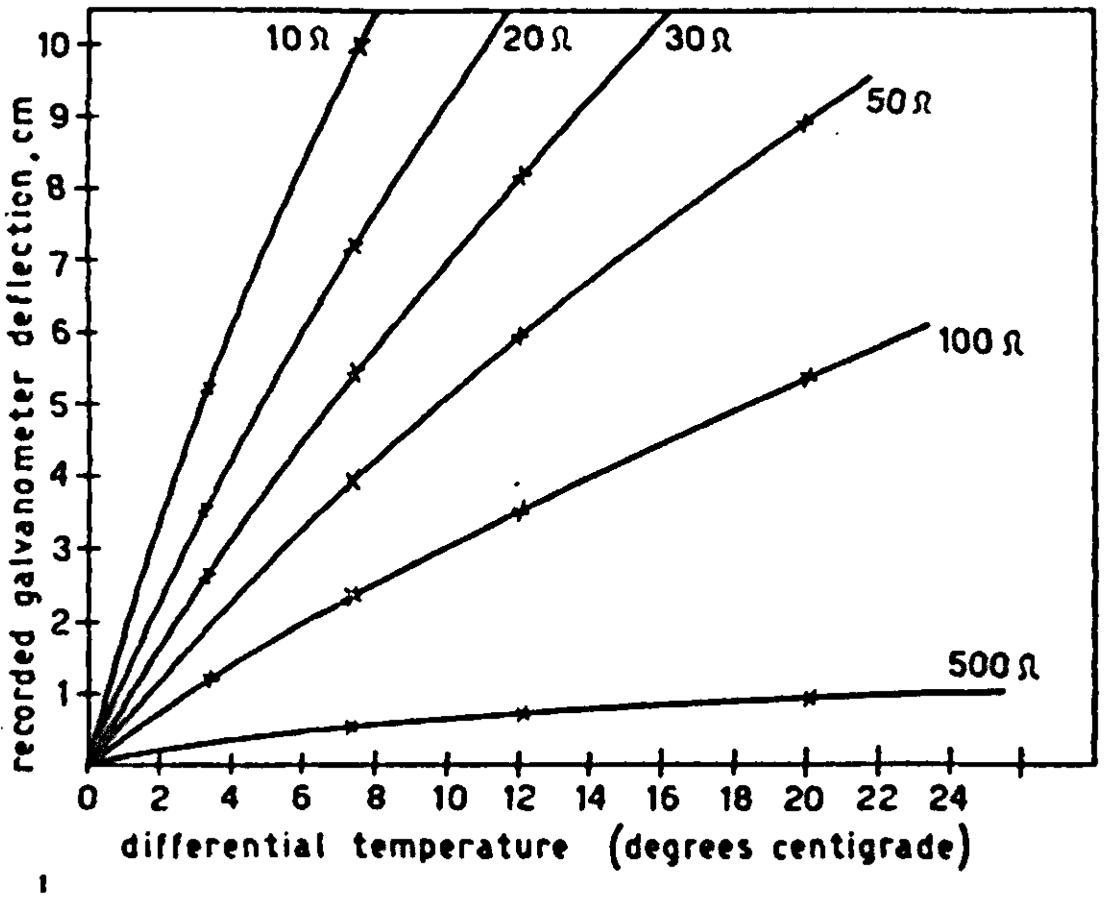


fig. 9. Plot of Δ T vs. recorded galvanometer deflection (cold junction at $10,5^{\circ}C$), for various sensitivity scales.

It should however be emphasized, that this calibration only holds for the low temperature range. As may be computed from the reference tables (142,180) of the Pt - Pt 10% Rh thermocouples, the e.m.f.. of the differential thermocouple for an observed difference of 20° in the range $10-30^{\circ}$ C is 0.11 mV, in the range $300-320^{\circ}$ C 0.19 mV, in the range $1000-1023^{\circ}$ C 0,23 mV. For accurate difference temperature measurements it is necessary to consider the dependency of Δ e.m.f. on temperature op to 1000oC.

The usefulness of the equipment.

For an appreciation of the usefulness of the equipment the following four items are of interest, viz. sensitivity, accurracy, reliability and practicability.

The sensitivity, expressed as the smallest quantity of any substance detectable in a mixture, is different for the various clay minerals, and has appeared to be strongly dependent on a great number of experimental conditions, as rate of heating, type of sample holder, thermocouple placement and sensitivity scale. The sensitivity may be raised or lowered appreciably by various means as is discussed in chapter 3.

The accurracy of the method depends in part upon the reading accuracy. With the photographic paper used the accuracy was (T ± 3) $^{\circ}$C for the furnace temperature readings. The accurracy of difference temperature readings varied according to the sensitivity scale used, but was always below 1 degree. The reaction temperatures of the different clay minerals mentioned in this study are always given in rounded values, so $573^{\circ}C$ is given as $575^{\circ}C$, $988^{\circ}C$ as $990^{\circ}C$, etc.

The reliability of the apparatus was tested by duplicating and triplicating the curves of various clay samples. In fig..8 a duplicated result is given of a kaolinite with 10% admixture of montmorillonite. The duplicability of the results is seen to be almost perfect. Most of the clays were run only one time for routine work. From time to time, however, duplicated analyses were made to check the reliability.

The practicability of the equipment turned out to be a function of various experimental conditions, as will be seen in the following chapter.

The materials used.

A number of clays was used as standard for checking purposes. Most of these were used in the experiments, described in chapter 3. The identity of these clays was verified by means of X-ray analysis, for which the writer is indebted to Mr. Drs. P.H.DAL (Keramisch Instituut T.N.O., Gouda) and to Mr. Dr.Ir.van der MAREL (Bodemkundig Instituut T.N.O., Groningen). All indications refer to clay separate ($< 2\mu$).

The standard clays used were the following:

Kaolinite, isle of Banka, Indonesia: obtained from the Keramisch Instituut, Gouda. Pure white, coarse crystalline sample, without admixture.

Kaolinite, Drybranch, Georgia, U.S.A.: obtained from Ward's Natural Science Establishment, New-York City. White, rather coarse crystalline sample, with a slight impurity of montmorillonite. References: 152, 174, 245.

Kaolinite, Les Eyzies, Dordogne, France: obtained from Mrs. S.CAILLERE, Paris. Pure white, coarse crystalline sample without impurities. References: 46.

Kaolinite, Zettlitz, Tschechoslovakaya; obtained from the Keramisch Instituut, Gouda. Pure white, coarse crystalline sample. Standard kaolinite of the Union de la Chimie pure et appliquee. References: 152, 245.

Halloysite, (hydrated) Mindesberg, Germany; obtained from Dr H.W.van der MAREL, Groningen. Pure sample, stored in a closed bottle.

Halloysite, var. indianaite, Bedford, Indiana U.S.A.; obtained from Ward N.S.E. Partial hydrated sample, pure white. References 6, 247.

Halloysite,	Djebel Debar, Algeria, N.-Africa; obtained from Mrs. S. CAILLERE Paris. X-ray photograph indicates a mixture of kaolinite and hydrated halloysite. References: 46, 91.
Montmorillonite,	Geisenheim, Germany. Very pure montmorillonite, poor in Mg and Ca.
Montmorillonite,	Osage, Wyoming U.S.A.; obtained from Ward's Natural Science Establihment . Rather pure sample, with some admixture of cristobalite. References: 228, 242, 282.
Montmorillonite,	Wyoming U.S.A. Standard sample obtained from City Chem. Corp. New-York. Pure sample, indicated as "Wyoming bentonite."
Montmorillonite,	Cadouin, Dordogne, France; obtained from Mrs. S. CAILLERE, Paris. Pure sample with pink colour. References:46,227.
Beidellite,	Burns, Mississippi U.S.A.; obtained from Dr. H.W.van der MAREL, Groningen. Pure sample.
Hectorite,	Hector, California, U.S.A.; Rather pure sample obtained from Dr. H.W.van der MAREL Groningen. References: 26, 88.
Illite,	Fithian, Illinois U.S.A.; obtained from Ward's Natural Science Establishment. Purified sample contains small amounts of quartz according to X-ray analysis.
Illite,	Winsum, Groningen, Netherlands; rather pure sample, with small amounts of quartz and montmorillonite.
Attapulgite,	Attapulgus, Georgia U.S.A.; obtained from Ward's Natural Science Establishment. Rather pure sample. References: 53, 76, 170, 182.
Vermiculite,	S-Africa; obtained from Dr. H.W.van de MAREL. Pure sample. References: 15, 143.
Quartz,	Moneta, Virginia U.S.A.; obtained from Ward's Natural Science Establishment. Very pure sample.
Quartz,	Germany; Merck's grade. Very pure.
Goethite,	Alban-le-Frayyse, France; obtained from Mrs S.CAILLERE, Paris. Very pure sample, coarse crystalline.

Gibbsite,	New Caledony, Australia; Very pure, coarse crystalline sample.
Gibbsite-Kaolinite,	Mungo, Surinam; obtained from Ir. J. VERHOOG, Paramaribo, Dutch Guyana. Mixture of gibbsite and kaolinite, coarse crystalline.

CHAPTER III

AN ACCOUNT OF THE FACTORS WHICH DETERMINE THE SHAPE OF DTA CURVES

§ 1. Introduction.

As outlined in chapter 1, there is much evidence to indicate that a great number of experimental conditions modify the shape of actually recorded curves of one and the same clay sample (12, 46, 147, 191, 219). Besides these experimental factors the nature of the clay is a decisive factor in the observed reactions. Thus in the enumeration of the factors determining the shape of DTA curves we may distinguish between experimental factors and clay factors. The experimental factors are determined by the conditions of the experiment; the clay factors, by the nature of the clay.

The several factors acting may be summarized as follows:

1. experimental factors
    - a. rate of temperature rise of the furnace;
    - b. nature of the sample holder;
    - c. depth and radius of the sample holes in the holder;
    - d. the places of temperature measurement of both furnace temperature and differential temperature;
    - e. nature and proportions of the thermocouples;
    - f. the nature of the inert substance (reference material for the differential thermocouple);
    - g. the tightness of packing of the clay and inert substance in the holes;
    - h. the effect of covering the sample holes;
    - i. the composition of the furnace-atmosphere.

2. Clay factors.
    - j. the particle size and the nature of the clay minerals present;
    - k. the degree of crystallization;
    - l. the cations adsorbed;
    - m. the presence of admixtures in the clay (salts, etc.).

Fortunately these factors are not all of equal importance. The recorded results are determined primarily by items a, c, d, g, h, i , j and k.

In the discussion of the relative influence of the two sets of factors above listed, three aspects of importance in the analysis should be distinguished. These are the influence of the factors upon the peak temperature, upon the reaction range and upon the intensity of the reactions (peak- height- and/or peaksurface.

The recording mechanism and equipment as a variable factor in the analysis is left out of consideration. It is self-evident that amplification of the e.m.f. of the differential thermocouple (21, 177) gives rise to an exaggerated picture of the DTA curves. This influence may be corrected easily.

Part I: Experimental factors.

§ 2. The influence of the rate of temperature rise.

HOULDSWORTH and COBB were the first to observe the influence of the velocity of temperature rise upon the measured reaction ranges of kaolinite. The greater the rate of temperature rise, the more the dehydration reaction at about 550°C was delayed. The same held for the exothermic reaction at about 980° C. In accurate static experiments PIETERS (237) observed that the dehydration reaction of kaolinite occured slightly above 430°C. Static experiments may be considered as having a rate of temperature rise zero. The dehydration curves published by NUTTING (224) indicate that the initiation of the dehydration reaction of kaolinite occurs at an even lower temperature (at about 380°C), the bulk of the H_2O vanishing at 500-510°C. These same observations were made by LONGCHAMBON (189). On the other hand, HAMILTON (120) and YURGANOV (285) note the initiation of the reaction as occuring slightly above 400°C, the bulk of the water vanishing at about 500°C.

In continuous dehydration experiments, carried out with an automatic recording thermobalance, MERVEILLE and BOUREILLE (210) and MUNIER (213) confirmed and extended the earlier observations of HOULDSWORTH and COBB. So it is not surprising that in DTA records this same lag of reactions is observed, the delay being more pronounced as the heating rate is increased (DE LEENHEER (187), SPEIL (271), ARENS (12)).

Experiments

In order to evaluate the influence of heating rate upon the recording of thermal reactions in DTA, a number of runs were made with the same sample of clay, but submitted to different heating rates in the furnaces I, II and III. For every set of observations the other variables (sampleholder, thermocouples, tightness of packing, etc.) were kept constant. The results are tabulated in table 2. See also fig. 19.

Table 2.

The influence of the rate of temperature rise of the furnace upon the observed peak temperatures, peak heights, peak ranges and peak areas of some reactions.

Sample	observed reaction	run no.	rate of heating °C/min.	peak temp °C	peak height mm	peak range min.	peak area mm^2
Kaolinite, Drybranch.	dehydration	100	6	545	18	14.0	630
	do	124	10	580	41	12.0	1230
	do	171	14	600	82	11.0	-
	do	135	16	610	86	10.2	2064
	do	157	19	620	96	10.0	2400
Kaolinite, Ranau.	do	128	9	565	20	12.0	600
	do	127	12	570	26	10.0	680
	do	202	19	590	70	9.2	1610
	do	193	22	595	85	9.2	1955
	inversion	128	4	970	8	8.4	168
	do	202	6	975	20	7.2	360
	do	193	11	975	28	6.0	420
Montmorillonite Osage.	dehydrat.	118	6	685	8	12.8	256
	do	136	14	700	19	6.8	323
	do	22	17	710	23	5.2	300
Halloysite, Mindesberg.	do	466	15	580	36	9.2	820
	do	467	29	610	70	4.8	850
Quartz, Moneta.	inversion	32	6	575	3	0.8	7
	do	116	12	575	5	0.5	10
	do	143	18	575	8	0.4	26
	do	225	21	575	12	0.5	36

It appears that considerable peak shifting occurs as a consequence of steeper heating rates. One should note here that measurements of the furnace temperatures were made in the clay sample itself, so that the reported peak temperatures refer to the temperature of the clay. The influence of measuring the furnace temperature in the inert substance will be discussed below in this same chapter; in these cases peak shifting is observed, amounting to about 90 degrees centigrade.

From the data it appears (see also fig. 19) that the heights of the peaks also depend on the velocity of temperature rise, steep heating rates being correlated with huge peaks. Furthermore the time of reaction, indicated as the peak range in the table, is also subject to variation, steep heating rates being correlated with small peak ranges. The peak range, however, may be expressed not only as the time of reaction but also as the difference between the temperature of expiration and the temperature of initiation. One sees that the temperature of initiation is lowered when the heating rate is lowered and the same holds, though to a lesser extent, for the temperature of expiration of the reaction.

The peak areas in different experiments with the same clay sample do not have a constant value, as appears from the figures. The present findings thus contrast with the observations of BERKELHAMER and SPEIL (26) and with the theoretical derivation of KULP. and KERR (174, 176). These workers used rather small variations in heating rates. One more interesting point follows from the data given and that is the constancy of the $\alpha \rightarrow \beta$-quartz inversion at 573°C. This reaction, because of its exceedingly rapid expiration and its accurate reproducibility, may be used as standard for calibration of the thermometer scale (BATES and PHELPS, 18), as has been described previously. If however the furnace temperature is measured in the inert substance, one may find as for instance KULP and KERR (177) did, a delay of this reaction. One should recognize that this delay is only apparent; it is caused by differences in heat flow in the inert substance and the reactant.

The peak temperature of the exothermal reaction of kaolinites at about 950°C is not noticeably affected by the heating rate, but the peak height, peak range and peak area are affected. However, a rather great varietal difference is observed in the appearance of this reaction if different kaolinites are compared. It is suggested below in this chapter that these differences may be ascribed to differences in the degree of crystallization (see also fig. 22).

Conclusions.

The effect of the rate of temperature rise upon the observed reactions in DTA may be summarized as follows:

1. There exists a systematic difference between the reactions

accompanied by loss in weight and those not accompanied by it;

2. Types of reactions accompanied by a loss in weight are strongly influenced by the heating rate; with increasing heating rate the peak temperature increases, as do also the peak height and peak area. But the peak range, measured as the time of reaction, decreases;

3. If the furnace temperature is measured in the clay sample types of reactions in which there is no loss in weight are not affected as regards peak temperature, but are affected as regards peak height, range and area;

4. From the results of experiments with varying heating rate, all other factors being kept constant, it is possible to compute empirically the reaction temperatures for zero rate of heating (static dehydration etc.). These „assymptotic" reaction temperatures are of importance for correlating DTA with dehydration curves.

§ 3. The influence of the sample holder.

Little is known of the effect of the nature of the sample holder upon the recorded DTA result, though, at least from a theoretical point of view, considerable influence might be expected. As all workers in this field use different types of sample holders there results considerable confusion.

Sample blocks differ among themselves in weight and specific heat, also in heat conductivity and in heat transfer coefficients. The greater the heat conductivity and heat transfer coefficient, the more rapid will be the calorie transport to the reactant during an endothermic reaction. As a consequence temperature gradients in the sample holder and between the wall of the sample hole and the place of temperature measurement will be minimized. Though the influence of heat transfer from block to reactants during any reaction has been recognized theoretically (VOLD, 276) never a comparison has been made between different containers.

Experiments.

In order to evaluate the influence of the nature of the sample holder, experiments were carried out with the sample blocks, c, d, g and j, keeping all other variables constant. In fig. 10 some curves are reproduced, obtained with the same clay material but submitted to the analysis in different blocks.

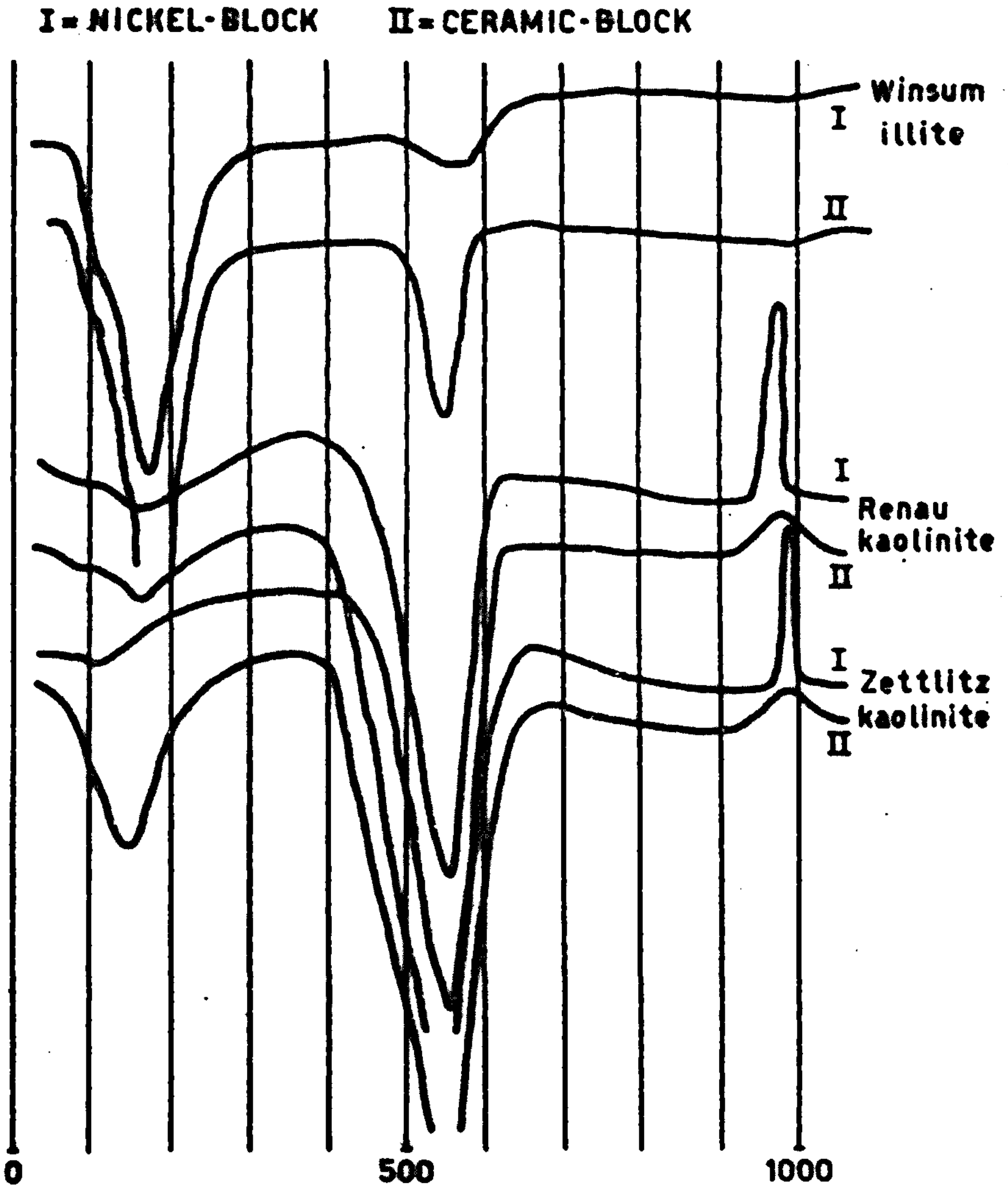


Fig. 10. The influence of the nature of the sample holder upon some DTA records.

The nickel blocks used has large heat conductivity coefficients and heat transfer coefficients as compared with the ceramic blocks. Some pertinent data for the materials in question follow: heat conductivity of nickel: $\lambda = 0.142$ cal sec^{-1} cm^{-1} degree C^{-1} at room temperature, and $\lambda = 0.068$ cal sec^{-1} cm^{-1} degree C^{-1} at 800°C; heat conductivity of alundum: $\lambda = 0.0022$ cal sec^{-1} cm^{-1} degree C^{-1} at room temperature and $\lambda = 0.0011$ cal sec^{-1} cm^{-1} degree C^{-1} at 800°C. These values were computed from HODGMAN (142) and LANGE (180).

From the curves given in fig. 10 it appears that ceramic blocks give rise to curves with relative sharp endothermic and faint exothermic reactions, while the opposite holds for nickel blocks. Thus it may be advantageous to use nickel blocks in cases, where weak exothermic phenomena are expected (hydrous iron oxydes), whereas ceramic blocks might be preferred in the case of clays exhibiting weak endothermal reactions (illites e.g.).

Conclusions.

From these and other observations the following conclusions were drawn.

1. Nickel blocks yield DTA curves with relatively flat endothermal and sharp exothermal reactions.
2. Ceramic blocks yield curves with sharp endothermal and relatively flat exothermal reactions.
3. All types of reactions undergo influences of the sample holder, irrespective of whether the reactions are accompanied by loss of material or not.
4. No noticeable peak shifting is observed.

§ 4. The effect of depth and radius of the sample holes.

This factor refers to a certain extent to the mass of clay material, taking part in the experiment, as it is determined by the volume V of the hole

$$M = \rho V = \pi r^2 h \rho$$

where M is the mass of clay material present, ρ is the apparent specific weight, r = radius and h = depth of the sample hole.

The volume V however appears to be a factor of minor importance, as regards reactions accompanied by changes in weight, The duration of any such reaction is preponderately determined by the velocity of escape of the originating gas (H_2O, CO_2) or of the entering gas (O_2 in the case of oxydation reactions). That the velocity of the gas stream is obviously affected by the depth and radius of the sample hole may be demonstrated for the decomposition of carbonates (150, 151, 286, 287). Huge endothermic reaction-records may be obtained, if the escape of originating gas is inhibited by sample containers having relative great depth compared to the radius. In such containers oxidation reactions (e.g. $4\ FeO + O_2 \rightarrow 2\ Fe_2O_3$) may be strongly inhibited, so that they are hardly observable. The unexplained behaviour of siderite ($FeCO_3$) and rhodochrosite ($MnCO_3$) in DTA records (BECK, 22; SPEIL, 271; KERR and KULP, 173; FREDERICKSON 89; CUTHBERT and ROWLAND, 61) probably is caused by mutual differences in depth and radius of the sample holes used. Unfortunately a number of investigators have failed to describe the sample blocks they used. The workers, who have operated with sample holes of relative small depth compared to radius have obtained the best records of the ferro-ferri reaction in siderite at about 730°C.

Experiments.

In order to study the influence of depth and radius of the sample holes, a number of runs were made with nickel-blocks (a, b, c, d and e) supplied with the same quantity of clay, all other variables being kept as constant as possible. The results of these experiments are given in table 3. It appears that in reactions accompanied by changes in weight, peak temperature, peak height and total duration of reactions are affected by varying radius and depth of the sample holes.

Table 3

The effect of depth and radius of the sample holes upon some curve characteristics.

Sample	Run no.	r mm	h mm	sample weight gr.	observed reaction	peak temp. °C .	peak height mm	peak range min.
Kaolinite, Banka.	219	3	12	0.080	dehydr.	555	52	8.6
	45	5	9	0.120	do	580	42	9.2
	260	6	12	0.120	do	585	70	9.0
	159	8	12	0.120	do	605	62	9.0
Kaolinite, Zettlitz.	281	8	12	0.150	do	575	74	12.0
	174	11	12	0.150	do	595	52	12.2
Quartz, Merck.	179	3	12	0.050	inversion	575	4	0.4
	145	5	9	0.050	do	575	3	0.4
	180	6	12	0.050	do	575	4	0.4
	74	8	12	0.050	do	575	6	0.4
Halloysite, Djebel Debar.	109	6	6	0.120	do	980	5	0.9
	211	8	12	0.120	do	985	7	1.0
	59	10	15	0.120	do	985	11	1.0

It appears from the data in table 3 that it is often advantageous to work with sample blocks supplied with deep and narrow holes, as for instance when making runs with micaceous materials, having small lattice water contents. Although the dehydration reactions may be enhanced in such cases, one should clearly realize that in these same runs certain other reactions may be overlooked. It is therefore advisable to run the same material successively in different sample holders, to be sure that no reaction is overlooked.

Conclusions.

From these and other data the following conclusions seem justified:

1. The depth and radius of sample holes greatly affect the appearance of thermal reactions accompanied by changes in weight, as regards peak temperature, peak height and total

duration of reaction.

2. Reactions not accompanied by changes in weight are not affected as regards peak temperature, and only slightly as regards peak height.
3. It is possible to mask or to enhance reactions, by varying the depth and radius of the sample holes.

§ 5. The effect of placement of the differential thermocouple junctions in the clay- and inert sample.

Closely related to the factor just discussed is the effect of placement of the thermocouple junctions in the respective materials. No systematic attempt has been made to reveal fully the effect, but in some experiments experience was obtained of its approximate magnitude. The effect in the low temperature range is different from the effect in the high temperature range. One remembers here that in the low temperature range heat transfer occurs largely by conduction, in the high temperature range by radiation. In general the following conclusions seem warranted

1. Deep placement of the differential thermocouple junctions in the samples yields DTA curves with relatively strong endothermic reactions in the low temperature ranges and flat endothermic reactions in the high ranges.
2. Exothermic reactions (in the high temperature range) are recorded the best with deep placement of the differential thermocouple.
3. For most reactions the thermocouple should be inserted in the samples without protective cover.
4. Thermocouples, fixed in the sample holders, are a great advantage as regards reproducibility of data.

§ 6. The influence of the nature and proportions of the thermocouples.

In the literature various types of thermocouples have been described. Most European workers operate with Pt - Pt 10% Rh thermocouples (CAILLERE and HENIN, MUNIER, WAEGEMANS, LEPINGLE, ROBERTS a.o.). These thermocouples are preferred on account of their durability. A disadvantage however is the relatively small e.m.f. being 9.57 mV at 1000°C (cold junction at 0°C). Therefore, in order to obviate the use of sensitive galvanometers for the differential temperature records, many American workers prefer the use of chromel-alumel thermocouples. These have an e.m.f. of 41.31 mV at 1000°C (KULP and KERR, JEFFRIES a.o.). The use of iron-constantan thermocouples, though having still greater e.m.f. at this temperature, is limited for routine work because of oxydation.

In the present study only Pt - Pt 10% Rh thermocouples have been used, but with varying wire diameters, viz. 0.2 mm and 0.5 mm. These sizes are in the range normally used. The heat capacity of the inserted wire was always small in comparison with the heat capacity of the clay (8×10^{-4}cal vs 4×10^{-2} cal for the 0.2 mm wire diameter). Although the differences obtained in the present records were only of minor importance, it is noted that WEB (unpublished results) obtained rather astonishing differences in recorded curves, obtained with various wire diameters, according to a personal communication of Dr S.B.HENDRICKS. The effect of wire diameter is expected to be great, when wire diameter is large in proportion to sample hole diameter, or when the heat capacity of inserted wire is great in proportion to the heat capacity of the clay sample and inert sample.

§ 7. The effect of the inert substance.

The inert material is as important for satisfactory DTA records as the clay material itself. Many different types of inert material are in use. Most workers use calcined alumina (Al_2O_3). British workers in this field (MACKENZIE, ROBERTS), and some French workers (e.g. MUNIER, LEPINGLE) prefer the use of fired clay, from the same sample as is to be investigated, as inert material. Both types of inert material have advantages and disadvantages.

The first requirement for any inert material is that it really be inert. That is to say, no reaction whatsoever may occur during heating. If calcined alumina is used in a number of successive experiments without replacement, it becomes more or less hygroscopic, depending on particle size. Since hygroscopicity of the inert substance may give the impression of an exothermal reaction in the clay sample in DTA records, the implication is that the calcined alumina should be replaced after each run, or at least after each two runs.

For satisfactory results the particle size distribution of the inert material should be approximately the same as in the clay sample. In some places rather coarse inert material is in use. The consequence is that there exists too big a difference in the contact heat conductivity between the clay and reference sample. This difference is the cause of considerable difficulty in obtaining a straight zero line.

Even the use of calcined clay prepared from the same sample being investigated is not without defects. For example, if the clay contains components with reversible thermal reactions, as for instance quartz, the appearance of such reversible reactions in the clay sample may be fully concealed. Moreover, it is not at all true that calcined clay has the same thermal properties (specific heat, heat conductivity, thermal diffusivity) as the original sample. Some thermal properties for kaolinite and calcined kaolinite (1000°C) are given in table 4.

Table 4.

Comparison of some thermal properties of kaolinite and calcined kaolinite.

	spec. heat cal $gr^{-1}\,{}^{o}C^{-1}$	heat conduct. cal cm ${}^{o}C^{-1}\,sec^{-1}$	thermal diffusivity $cm^2\ sec^{-1}$
kaolinite	0.201	$0.72 \cdot 10^{-3}$	
calcined kaolinite	0.428	$1.6 \cdot 10^{-3}$	

It appears from the data in table 4 that on thermal evidence alone one is not warranted in using calcined clay as inert material. The only advantage is that particle size distribution of both clay and inert substance is approximately the same.

Another aspect, which should be considered under this heading, is the place where the furnace temperature is to be measured. In most experiments described in the literature furnace temperature is measured in the inert material and not in the clay, this being the cause of rather considerable shifts in peak temperatures.

MACKENZIE (191) pointed out that temperatures measured in inert materials should be corrected to clay temperatures in order to facilitate calculations. In order to avoid complications, however, it would appear preferable to measure the furnace temperature always in the clay sample itself.

Experiments.

In this study a number of runs were made, with the furnace temperature thermocouple placed in the inert sample (normally the furnace temperature was measured in the clay). Moreover different types of inert material were used. In one blank experiment with calcined alumina from a foreign source, a rather sharp endothermic reaction at about 220°C was observed, indicating the presence of some hydrous Al-oxyde. It is absolutely neccessary to test the inertia of the reference material after each renewal.

The influence of the measurement of furnace temperature in the inert substance upon the peak temperature of some reactions is summarized in table 5. From the figures given it appears that all types of reactions undergo peak shifting when furnace temperature measurements are made in the reference material. The amount of peak shifting, however, is different for the various materials.

Table 5

Apparent peak shifting as a result of measuring the furnace temperature in the inert substance.

Sample	Sample holder	heating rate °C/min.	Peak temperature °C		Difference (peak shift.)
			measured in clay	measured in inert mat.	
Kaolinite, Drybranch	d	6	540	545	5
	d	14	550	600	50
	d	19	555	620	65
Kaolinite, Banka.	d	7	560	560	0
	d	12	565	580	15
	d	21	570	605	35
Quartz, Moneta.	d	6	575	575	0
	d	12	575	585	10
	d	18	575	590	15
	d	21	575	600	25

The peak shifting observed may be explained qualitatively by mutual differences in thermal conductivity of clay and inert material.

Conclusions.

The following conclusions may be drawn.

1. The inert material should have thermal characteristics (spec. heat, heat conductivity, thermal diffusivity) as

closely equal as possible to those of the clay. This requirement is never fully realizable, because the thermal characteristics of clay undergo rather sudden changes, accompanied with the reactions.

2. If furnace temperature is measured in the inert substance an apparent peak shifting is observed, the amount of which is increased with increasing radius of sample hole and increasing heating rate. This holds for all types of reactions.
3. It is recommended that furnace temperature be measured in the clay sample.
4. The use of calcined clay, of the same sample as is to be investigated, as inert material, has no fundamental advantages over the use of calcined alumina, provided particle size distribution of the latter is not different from the clay.

§ 8. The effect of tightness of packing of clay and inert substance in the sample holes.

The evaluation of the effect of packing on DTA recordings is rather difficult, though the effect itself is obvious. It is not easy to get reproduceable loose packings and this is the reason that very hard packing, or very loose packing (obtained with loose sprinkling of the materials in the respective holes) are most commonly used.

The effect of packing may be reduced to three causes: differences in sample weights, in heat conductivity and in thermal diffusivity. In the low temperature ranges, where heat transfer is governed principally by conduction, the effect is the most pronounced. In the high temperature ranges the effect may fully disappear as heat transfer is there determined principally by radiation.

Experiments.

A number of experiments were made with different types of packing of clay and inert substance in the sample holes (fig. 11), while all other factors (sample holder, weight of sample etc.) were kept as constant as possible.

In experiments with loose packing (relative great porosity), the heat transfer from the sample block to the thermocouples in the middle of the holes, is inhibited, because of the very small heat conductivity coefficient of the air enclosed. As a result one finds in the recordings endothermic reactions, which are faint compared with those observed for tight packings. The effect on exothermic reactions is in the same direction, though the effect is less pronounced.

The most marked differences originate, if clay sample and inert sample are packed differently. If the clay is packed tightly and the reference material very loosely, one may find an „exothermic" deviation from the zero line of the differential temperature recording galvanometer. The deviation is of unpronounced character and over a rather wide temperature range (see curve 207 in fig. 11). This same effect may be obtained if inert material with a very low coefficient of heat conductivity is used. The opposite effect, an „endothermic" deviation of the differential temperature line over a wide temperature range (up to about 600°C), may be observed if the clay is sprinkled loosely in the sample hole while the inert substance is packed tightly (see curves 198, 197 and 202). In fig. 11 some pronounced examples of these effects are given.

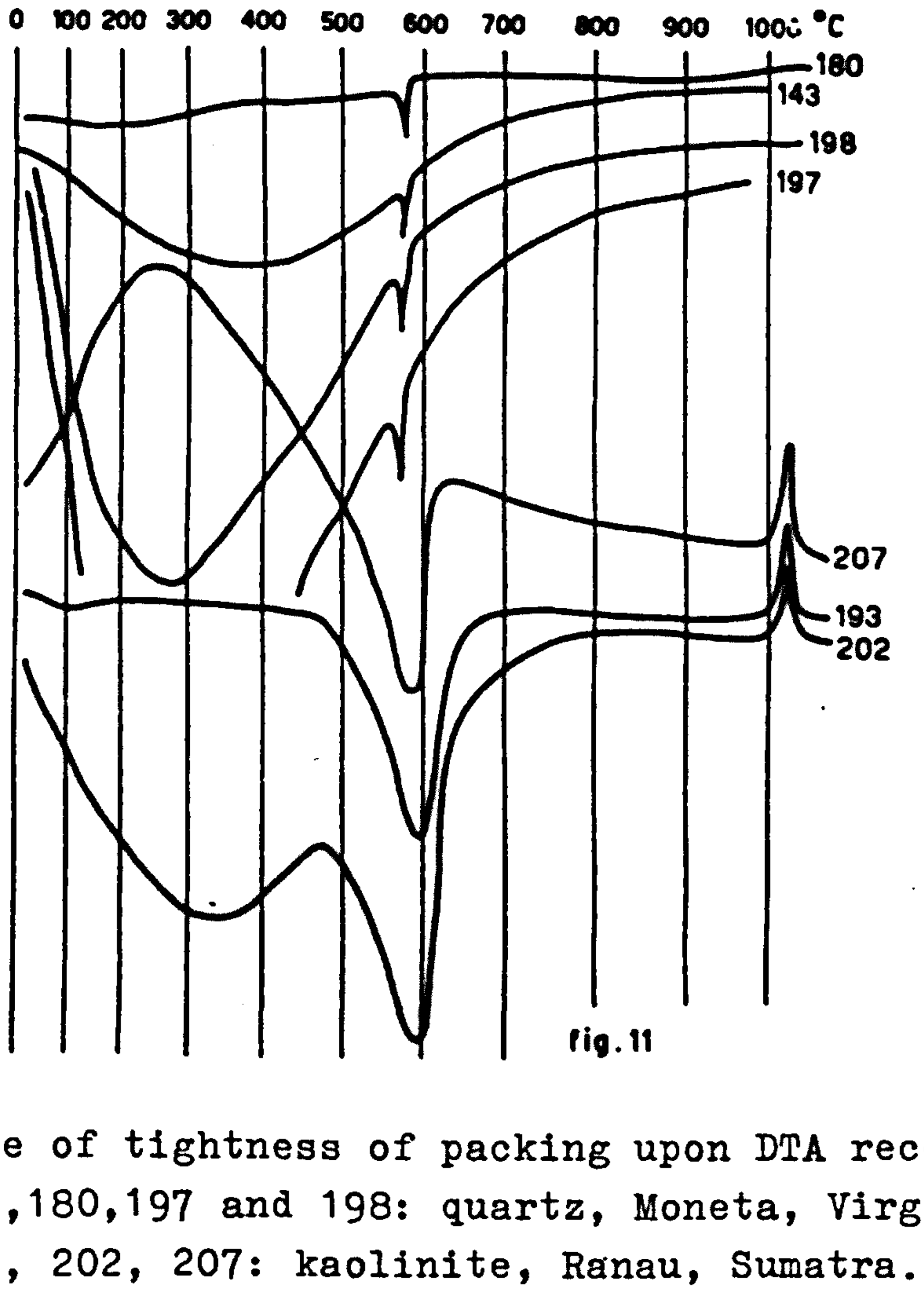


fig.11

The influence of tightness of packing upon DTA records.
Runs no. 143,180,197 and 198: quartz, Moneta, Virginia.
Runs no. 193, 202, 207: kaolinite, Ranau, Sumatra.

Conclusions.

The following conclusions may be drawn.

1. Differences in density of packing are the most common cause of deviations from straight zero-lines in ranges where no reactions occur.
2. Hard packing, since it is the easiest to reproduce, is recommended for most cases, to obtain recordings with pronounced reactions and with straight zero lines.
3. Loose packing gives rise to faint reactions, the effect lying in the same direction for all types of reaction, except probably the oxydation reactions.

§ 9. The effect of covering the sample holes.

Covering of sample holes is often desired to avoid direct radiation into the samples, as an aid to get straight zero lines.

The covering however influences the composition of the gaseous phase in the reaction environment. All reactions of the type

$$\underset{\text{solid}}{AB} \longrightarrow \underset{\text{solid}}{A} + \underset{\text{gas}}{B}$$

and

$$\underset{\text{solid}}{R} + \underset{\text{gas}}{O_2} \longrightarrow \underset{\text{solid}}{RO}$$

are to a certain extent equilibrium-reactions; hence their expiration is greatly determined by the rate of escape of the formed gas, or by the rate of entrance of the reacting gas.

The first type of reaction is inhibited by covering, the reaction temperature being then strongly shifted upwards; the second type of reaction is not perceptible at all in DTA records, if the reaction vessel is covered. The quantitative evaluation, however, of the peak shifting in the first type of reactions is hardly possible.

Reactions of the type

$$\underset{\text{solid}}{A} \longrightarrow \underset{\text{solid}}{A'}$$

are not materially influenced by covering, as regards peak temperature and intensity of the reactions.

Experiments.

In furnace III a number of runs were made with the same nickel block, to compare the effect of covering and uncovering.

In fig. 12 some results are given. It is seen that the dehydration reactions are enhanced by covering whereas inversion reactions are not affected.

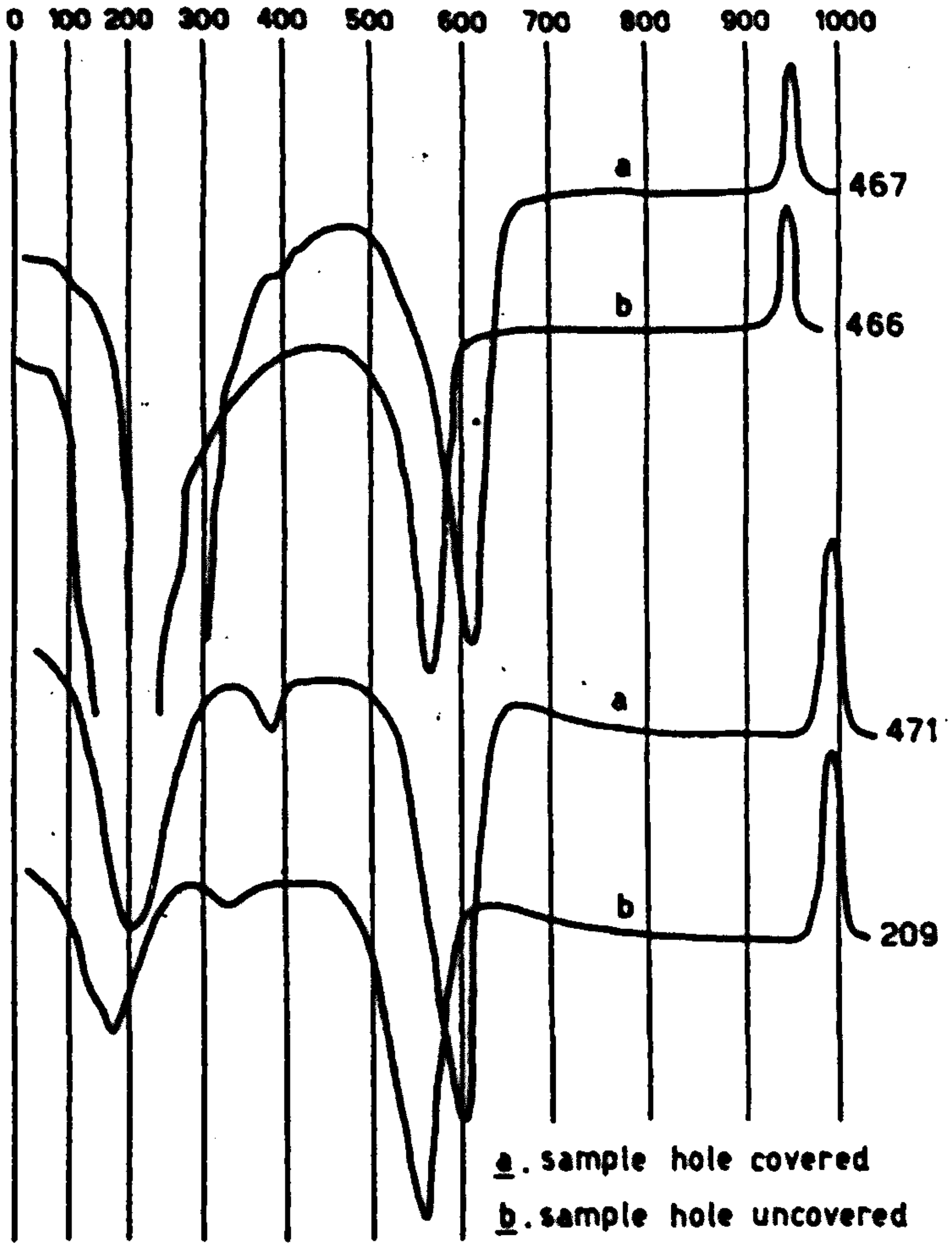


fig.12

Runs of halloysite, Mindesberg, Germany (no. 466,467) and of indianaite, Bedford, Indiana U.S.A. (no. 471 and 209).

It has been previously indicated in this chapter that the appearance of the oxidation reaction in siderite ($FeCO_3$) may be strongly affected by depth and radius of the sample holes. BECK (22) showed that covering of the sample holes could have the same effects. For clays, in which oxidation phenomena are expected upon heating, there should be a liberal acces of oxygen.

In the case of the DTA of siderite and rhodochrosite there is a dilemma. The reaction takes place in two steps:

$$FeCO_3 \rightarrow FeO + CO_2 \quad \text{(endotherm)}$$
$$4\ FeO + O_2 \rightarrow 2\ Fe_2O_3 \quad \text{(exotherm)}$$

The first mentioned reaction may be enhanced by covering the sample hole. Then reaction peaks occur at higher temperatures. The second reaction may be fully masked by covering. With uncovered sampleholes, on the contrary, the first reaction appears less pronounced, while the second is well developped. It is more or less a matter of personal choice and other experimental conditions, which reaction should be favoured.

Conclusions.

1. Covering the sample holes excert considerable influence upon the appearance of reactions, when there is a change in weight of the reactant.
2. Reactions, accompanied by loss in weight (dehydration, loss of CO_2) may be enhanced by covering, while a peak-shifting upwards occurs.
3. Reactions accompanied by gain in weight (oxidation), may be fully inhibited by covering, or may be of a fully unpronounced character.
4. Though covering may aid in certain cases to obtain straight zero lines, it should be avoided for general prospecting purposes.

§ 10. The influence of the composition of the furnace atmosphere.

In the same way as covering of the sample holes affects the appearance of thermal reactions, the composition of the furnace atmosphere excerts its influence. Generally this factor is overlooked in the carrying out of dehydration- or of other thermal experiments.

For the dehydration reaction of kaolinite, PIETERS examined very accurately, in a number of static experiments, the influence of the partial vapour pressure of water in the furnace atmosphere upon the reaction temperature. His result are given in fig. 13. It is seen that the temperature of the dehydration reaction increases with increasing partial vapour pressure of water on the furnace atmosphere.

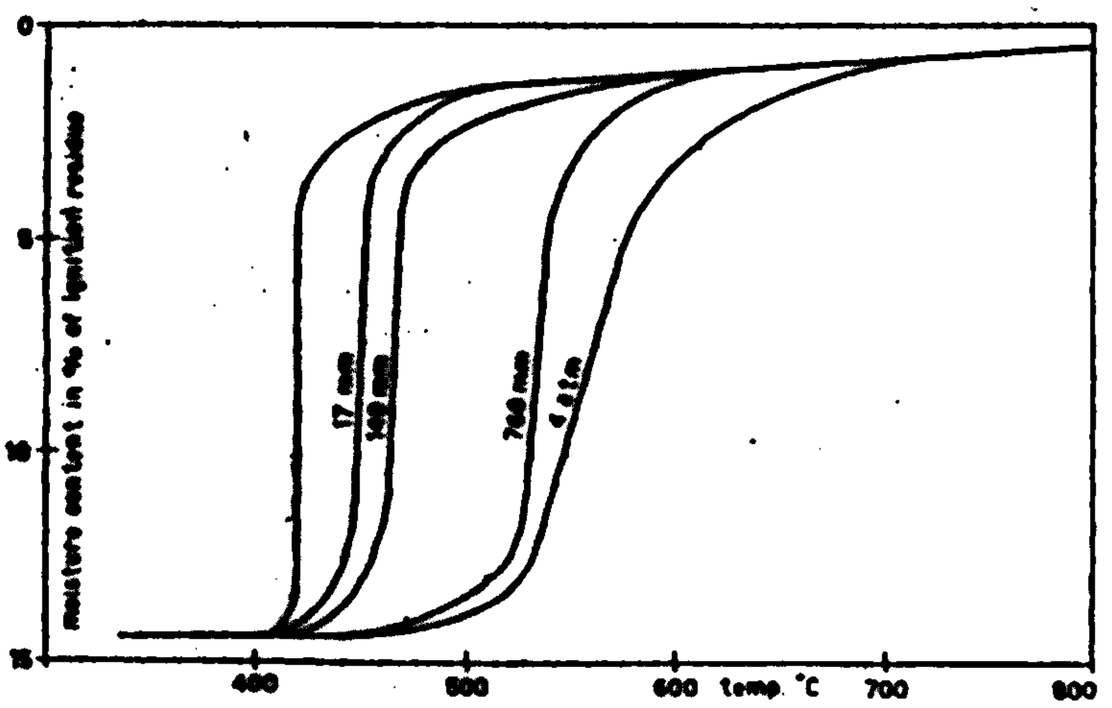


fig. 13. Dehydration of Zettlitz kaolinite as a function of the partial vapour pressure of water in the furnace atmosphere (from PIETERS, 237).

In air of average composition in Holland, the partial vapour pressure of water is about 11 mm mercury pressure (70% relative humidity) at room temperature (18°C). This vapour pressure may in itself account for a delay of the dehydration reaction of kaolinite amounting to 30 - 40 degrees. Approximately the same holds for the dehydration reactions of other minerals. In so far as known the factor of relative humidity has never been considered, in explaining shifts in reaction temperatures in DTA.

The atmosphere in the furnaces used in this study were not controlled as to composition of the air, though this is considered desirable for accurate analyses.

As regards carbonates, considerable attention has been given to the decomposition reactions in dependence of the composition of the environmental atmosphere (HEINZ, 151; HUTTIG, 150 and ZAWADSKI, 286 a.o.). Here too a close relationship is found between the decomposition temperature and the partial vapour pressure of CO_2 in the reaction atmosphere. The reaction may be delayed considerably in environments of relative high CO_2 pressure.

Analogous considerations hold for oxydation reactions. If the furnace atmosphere is deficient in oxygen, these reactions may be inhibited.

For certain purposes (as for the inhibition of the oxydation of organic matter) it is practicable to control the furnace atmosphere composition (ROWLAND and JONES). For such experiments a nitrogen atmosphere may be applied. In so far as known, DTA records in vacuum have never been carried out. Some static (dehydration) experiments carried out in vacuum indicate the lowering of reaction temperatures accompanied by great reaction velocities.

The following conclusions may be drawn.

1. The composition of the furnace atmosphere affects considerably the initiation and course of reactions accompanied by changes in weight.
2. The initiation and course of dehydration reactions are influenced by the partial vapour pressure of water. The decomposition reactions of carbonates are influenced by the partial vapour pressure of CO_2 and the oxydation reactions are influenced by the partial vapour pressure of O_2 in the furnace atmosphere.

Part II: The clay-bound factors.

§ 11. The nature of the clay mineral(s) present.

As has been shown above, many apparatus-bound factors may affect the result of thermal analysis; but these influences bring about in most cases only modifications of the primary pattern, which is determined by the nature of the clay. If this were not so, DTA should be unsuitable for clay mineral analysis.

The dehydration temperatures and the heats of reaction are specific for the different clay minerals. The thermal stability of crystals depends primarily on binding energies within the crystal lattices. As temperature increases the trend towards increasing the entropy and decreasing the energy of the crystal lattice is manifested.

The result is the decomposition of the crystal at a distinct temperature.

What interests us primarily here, is the mutual influence of clay minerals upon the appearance of thermal reactions. As was observed in the DTA records of artificial mixtures of clay minerals (AGAFONOFF, 1; CAILLERE and ORCEL, 227; CAILLERE, 41; GRIM, 99), a rather considerable peak shifting may occur as a consequence of mixing. The reaction temperatures of the components in the mixture are not the same as the reaction temperatures of the pure components of the mixture. The mutual influence of the components in the mixture has been considered as being analogous to the lowering of melting points of pure components by the addition of admixtures (227). However, the reaction temperatures are not systematically lowered in DTA, but sometimes increase by the presence of admixtures. There exists consequently a fundamental difference between the two phenomena.

Another point which should be considered is the particle size of the clay. KELLEY and coworkers (163, 165) were the first to reveal the influence of grinding of clays upon their dehydration. They found that prolonged grinding result in a breakdown of the crystal lattice. PERKINS (233) made a number of similar experiments. The DTA curves in his publications indicate a decreased intensity of reaction with increased time of grinding. Prolonged grinding lead to a very smooth curve which had no pronounced peaks. Analogous effects of the break-down of clay minerals after prolonged grinding were recorded with X-ray analysis by JACKSON and TRUOG (153) and with DTA by SPEIL (271) and by KULP and KERR (174) with ground dickite.

Unlike the effects of fine grinding, just mentioned, increasing particle size of the sample results in strong reactions for the reactions accompanied by changes in weight. The rate of such reactions is controlled largely by diffusion, and should therefore obey to a certain extent the laws of diffusion. Thus the rate of water-loss during dehydration should depend upon the sum of the surface-area of the particles, according to the law of FICK $dm = D \cdot a \frac{dc}{dx} dt$ where dm represents a small quantity of water, passing during a time-interval dt through a surface area <u>a</u>, over a concentration gradient $\frac{dc}{dx}$. The diffusion constant D is a constant of the material.

As is well known for a given weight of material the sum of the surface area of particles increases with decreasing particle size. If particle size is greater than about 20 μ, the surface area is too small for dehydration reactions to occur rapidly enough to yield pronounced reaction effects in current DTA. Thus, when the average size of particles is 20 μ, recorded reactions are faint and are spread over a rather wide temperature range.

Fortunately no clay minerals occur in fractions larger than about 5 μ. But for DTA records from ordinary minerals (muscovite, chlorites, vermiculite, feldspars etc.) the limiting value of particle size for pronounced reactions should be considered.

It is obvious that for reactions of the inversion type

$$\text{solid } A_1 \rightleftharpoons \text{solid } A_2$$

the considerations of particle size do not hold. For example quartz of diameter 200 μ still shows perfectly the $\alpha \leftrightarrow \beta$ inversion.

§ 12. The effect of degree of crystallization.

Not all clays consist of perfectly crystallized clay minerals. SEDLETSKII (261, 263) was one of the first to call attention to the presence of mutabilites and metastabilites in soil clays. These forms are the products of transition between precipitates in the soil solution and clay minerals.

Precipitates in the soil solution may be imperfectly crystallized as a consequence of the conditions of the environment (principally low temperature and low atmospheric pressure). Through aging and the intermittent wetting and drying the imperfectly crystallized clay minerals may gradually convert to better crystallized bodies. The process might require ages and ages, depending on constancy of environmental conditions. According to these viewpoints, clay formation would start with the badly crystallized bodies in the average soil, as was pointed out by EDELMAN and SCHUFFELEN (75).

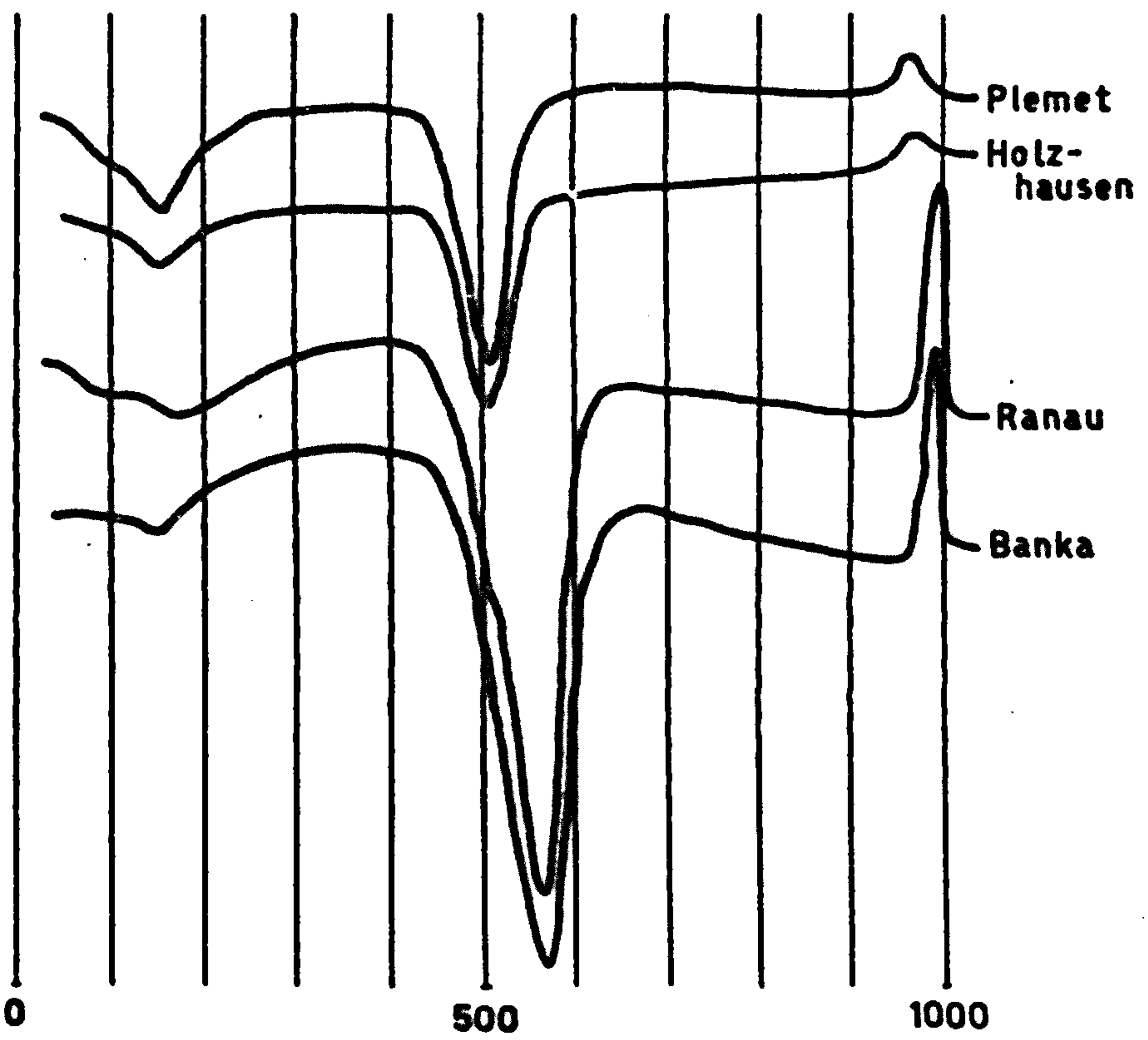
A well-known example of a clay-mineral of the poorly crystallized type is the fire-clay mineral, closely related to kaolinite, and described independently by FAVEJEE (84) and GRIM (105). According to BRINDLEY and coworkers (34, 36, 37) the fire-clay mineral should be a transition type between hydrated halloysite and kaolinite. In so far as thermal curves may serve as additional evidence, there is an indication that Brindley's view-point is correct; see fig. 22.

Experiments.

To cover the influence of the degree of crystallization, a number of runs were made from well and poorly crystallized clay minerals, whether occurring in nature (kaolinites etc.) or artificially prepared (iron and aluminium-hydroxydes).

In fig. 14 and 22 the differential thermal curves of some good crystallized kaolinites (Zettlitz, Banka) are compared with the curves of hydrated halloysites (Mindesberg, Bedford) of fire-clay-minerals (Plemet, Holzhausen) and of a kaolinite-halloysite mixture (Djebel Debar). The intermediate position of the fire-clay minerals is obvious, as regards the general shape of the curves (fig. 22). However, the poorly crystallized types are characterized by a shifting of reactions to lower temperature ranges. The reaction intensity is rather low at the same time.

This reaction shifting, in dependence on degree of crystal-



DTA curves of some well and badly crystallized kaolinites.

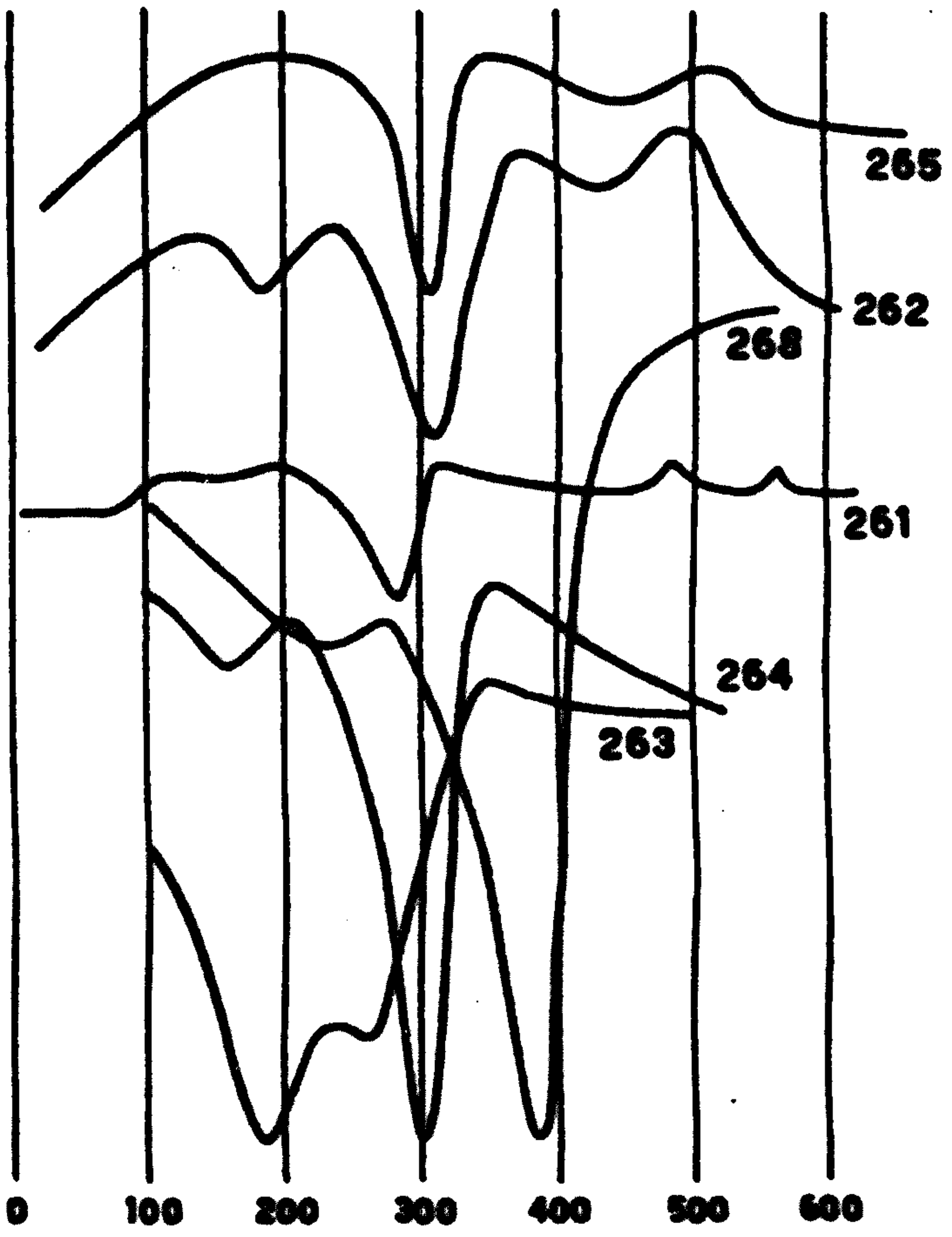


fig.14a

lization, has been observed by SCHUYLENBORGH and ARENS (259) with a number of hydrous iron-oxydes. The better the crystallization is, the higher is the reaction temperature. Fig. 14^a shows a number of curves from natural and artificial prepared hydrous iron oxydes. The curves No. 265 and 268 are from well crystallized bodies, the other curves from poorly crystallized ones. In the latter cases the reaction temperatures are lowered and the peaks are of small intensity. The description of the preparation of a range of hydrous oxydes with different degree of crystallization is given in several papers of SCHUYLENBORGH (256-259). The concentration of the starting solutions, the time and the temperature of the precipitation appear to be decisive for the degree of crystallization, as is well-known from the analitical chemistry.

Analogous observations of peak shifting in dependence on crystallization were made by CAILLERE and HENIN (47, 48), in experiments with natural and synthetic antigorite. The badly crystallized synthetic product showed the same general shape of curve as the natural, well crystallized, body, but peak temperatures of the former were shifted about 200 degrees centigrade downward.

Conclusions.

Summarizing the effect of degree of crystallization, it may be stated that the appearance of reactions is exceedingly affected by the degree of crystallization. The better the crystals are grown out, the higher will be the decomposition temperature. Both endothermic and exothermic reactions are affected.

§ 13. The effect of the adsorbed cations.

One of the properties of clay, discovered hundred years ago by THOMPSON and WAY (66), is its capability to adsorb cations.

The different clay minerals, however, vary among themselves in exchange capacity. In table 6 the exchange capacity of some clays, used in this study, is given. The determinations were made with the percolation-technique of HUDIG and ROBORGH (240) and described by VAN DER MAREL (200).

Table 6.
Exchange capacity of various clay minerals.

Name and location	Exchange cap., pH=6.5 m.e. per 100 gr.
Kaolinite - Banka (no. 59)	6.5
Kaolinite - Drybranch	7.3
Halloysite-4 - Pekalongan (no. 25)	28.0
Illite - Winsum	29.0
Montmorillonite - Osage	83.1
Montmorillonite - Geisenheim (no. 46)	78.8
Montmorillonite - Wyo. bentonite (no. 3)	54.1
Vermiculite - S.Africa (V)	130

As the adsorbed cations are hydrated, it is to be expected that these will affect the DTA curves. HENDRICKS, NELSON and ALEXANDER (139) proved this for a number of montmorillonites saturated with various cations. In the low temperature range (0-300°C) of the curves of montmorillonites there may be distinguished two peaks (see fig. 1). One peak stems from the hydration water of the clay mineral itself (interlayer water) and one originates from the hydration water of the adsorbed cation(s). The magnitude of this latter peak is subject to the hydration of the adsorbed cation. According to HENDRICKS and coworkers the hydration is as follows. Mg, Ca, Sr and Ba appear to be the most hydrated, they have about 6 watermolecules of hydration water per ion. Next comes Li with 3 molecules of hydration water. Finally there are H, K, Na, and Cs with one or no molecules of hydration water, according to HENDRICKS c.s. These results are critical reviewed by FORSLIND (87).

Similar experiments of the influence of the nature of the adsorbed cations upon DTA results were made by CAILLERE, HENIN and TURC (43, 44). They found an Al-saturated complex in certain cases to be advantageous, because a more pronounced curve could be obtained with it. The presence of iron in the exchange complex was found to flatten the peaks (see ORCEL, 226 and CAILLERE and HENIN, 45).

As regards the nature of the adsorbed cations, vermiculites are the most sensitive, both with respect to DTA response and to X-ray analysis, as was revealed by BARSHAD (15, 16, 17) and WALKER (278, 279). It appeared from X-ray and DTA records that natural vermiculite, which is probably Mg OH^+-saturated, could be converted to biotite by K-saturation, as Ca- and Ba-vermicu-

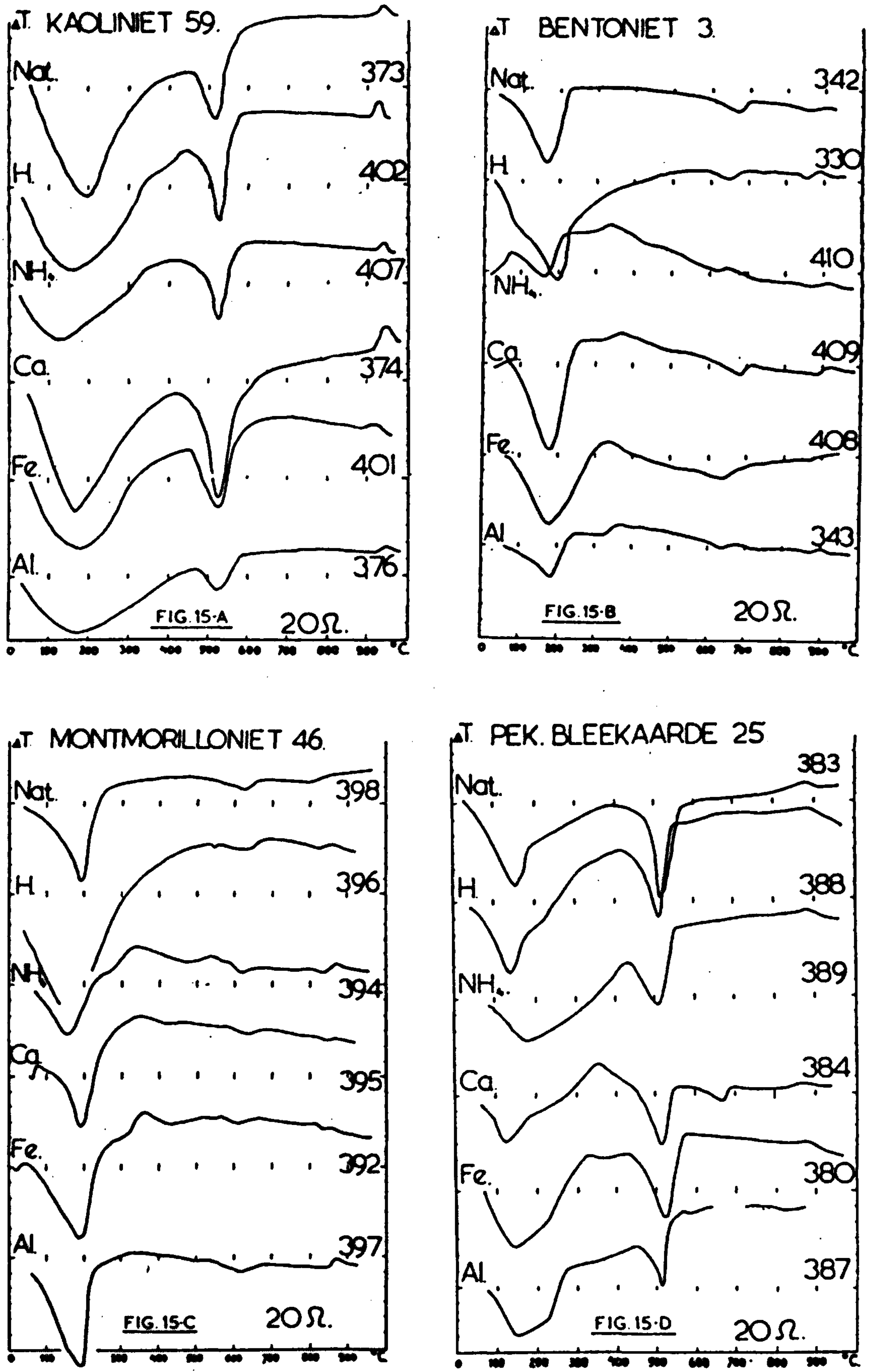


Fig. 15. DTA curves of kaolinite (Banka 59), Montmorillonite (Wyo, bentonite no. 3 and Geisenheim no. 46) and from a bleacking clay (Pekalongan), saturated with various cations.

lites on the other hand behaved like the original natural body. But NH_4-saturated vermiculite reacted totally different. WALKER (279) pointed out that saturation with Sr^{++}, Ca^{++}, Mg^{++} and Be^{++} gives rise to the most hydrated vermiculite-complex. Next comes saturation with Na^+ and Al^{+++}. Li^+ complexes are still less hydrated; NH_4^+ and K^+ saturation leads to the least hydrated form.

Another item, which should be sonsidered in this section, is the influence of the presence of organic cations, in so far as these oxydize and decompose during heating. DTA records of clays saturated with complexes of organic cations have been made by ALLAWAY (9) and BRADLEY and GRIM (31). In clays with relative high' adsorbtive capacities, saturation with organic cations may serve in the additional characterization of the nature of the clay mineral, e.g., in the distinction of beidellite, saponite, hectorite and montmorillonite, and in the distinction of these from micaceous clay minerals.

Experiments.

A number of experiments were made with clays, saturated with different cations, to reveal the influence of the adsorbed cations. To saturate the complex with the various cations, clay separates were treated 5 days with excess 0.1 n solutions of the chlorides of Fe, Al, Ca, Mg, NH_4 and Na and 0.05 n HCl respectively. Subsequently the clays were brought into cellophane bags and dialyzed until no more free chloride could be detected in the outer solution. The clays were then dried, first on a steam bath, and, subsequently, in a thermostat at 105°C.

The results of the DTA runs are recorded in fig. 15^{a-d} and 16^{a-b}. It appears that the clays with the smallest exchange capacity (kaolinites) are the least affected by the variations in adsorbed cations, except in the case of Fe and Al. The hydrogen saturated clays give rise in most cases to the most pronounced curves. From the NH_4-saturated clays it was difficult to obtain reproducible results. With these clays, heating causes the transition

$$NH_4\text{-clay} \longrightarrow H\text{-clay} + NH_3$$

which is a reaction in addition to dehydration. Probably this additional reaction may account for the exceptional thermal behaviour of NH_4-clays. In the higher temperature ranges the NH_4-clays behave as H-clays, as regards thermal reactions.

The curves of montmorillonites and vermiculites are affected most by the cations adsorbed. Since saturation with Ca and Mg gives rise to a double-peaked endothermal reaction below

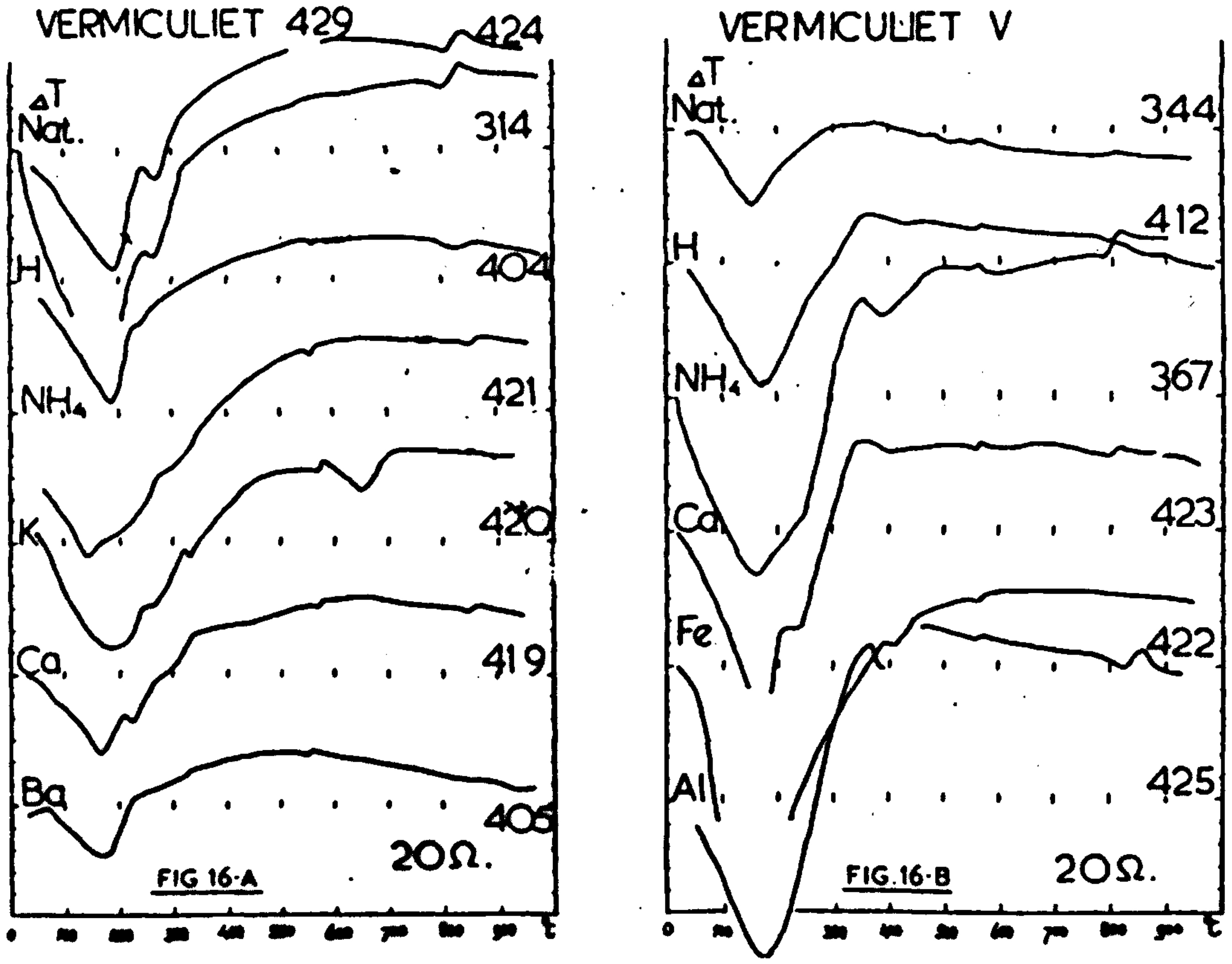


fig. 16. DTA curves of vermiculites, saturated with different cations.

300°C, this character might serve to distinguish between Na- and K-montmorillonites, and Ca- and Mg-montmorillonites. The former show only a single-peaked reaction below 300°C.

Conclusions.

From the present observations and from observations quoted from literature, the following conclusions are justified.

1. The effect of the nature of the adsorbed cation is of increasing importance with increasing exchange capacity. The effect is smallest for kaolinites and the most pronounced for vermiculites (fig. 15 and 16^{a-b}).
2. Saturation of the clay with hydrogen (by means of repeated treatment with hydrochloric acid in a concentration not exceeding 0.05 n) yields the most pronounced DTA curves for all minerals investigated.
3. Saturation with Fe^{+++} or Al^{+++} in most cases flattens the curves, even with kaolinites.
4. Ammonium saturation gives rise to an additional reaction

$$NH_4\text{-clay} \rightarrow \text{H-clay} + NH_3.$$

5. In montmorillonites Ca^{++} and Mg^{++} saturation leads to double -peaked endothermal reaction in the low temperature range.
6. Treatment of clays with organic cations may facilitate the distinction of clay minerals, especially in the case of the montmorillonites.

§ 14. The effect of the presence of admixtures.

The presence of salts may seriously interfere with the normal course of DTA curves.

CAILLERE and HENIN (46) showed how DTA curves were modified for various clay minerals, treated with $Al(NO_3)_3$, $AlCl_3$, $(NH_4)_2CO_3$ and K_2SiO_3. The treatment with $Al(NO_3)_3$ generally resulted in a more pronounced DTA curve for montmorillonites (except nontronite) and for illite-bravaisite. On the other hand this same treatment flattened the curves of anauxite and attapulgite-palygorskite. Kaolinites treated with $AlCl_3$ showed a pronounced exothermic reaction at 950°C. The curve of nontronite could be improved by treating the clay with $(NH_4)_2CO_3$. Treatment of montmorillonite with potassium silicate resulted in curves which were more pronounced.

GRUVER and coworkers (117) observed the reactions of kaolinites after mixing with sodium chloride and sodium carbonate. A 2% and still more a 5% admixture of carbonate resulted in considerable reduced reaction rates, as was evidenced by flattening of the curves. NaCl only affected the curves if present in quantities as high as 5% or more. For the decomposition reactions of carbonates similar observations were made by ESIN, GEL'D and POPEL (77). These reactions likewise are subject to considerable modification, due to the presence of salts.

Organic admixtures may considerably interfere in DTA records. AGAFONOFF and JOURACSKY (2) observed that normal soil organic matter was decomposed between room temperature and 600°C in thermal analysis experiments. The decomposition reaction is essentially exothermic, but spread over a rather wide temperature range. The same observations were made by CAILLERE and HENIN (46). BRADLEY and GRIM (31) found the decomposition of various amines, with which the clay was treated, to take place in distinct temperature ranges, but always below 600°C. In particular the curves of montmorillonites could be considerably modified. The work of ALLAWAY (9) has been quoted previously.

Experiments.

In some experiments glycerol treated clays (prepared according to the technique devellopped by MACEWAN (190) for X-ray analysis) were submitted to DTA. With kaolinite and illite no additional reaction was found, as was expected; while montmorillonites showed an additional exothermic peak (fig. 17). In another set of experiments some methylated clays, prepared according to the technique of BERGER (23), were submitted to DTA. The decomposition of the bound methoxyl groups resulted in an additional exothermic reaction in montmorillonites. The glycerol-solvation of clay minerals, previous to differential thermal analysis, is another means for distinguishing the montmorillonite clays from the illites, the former being subject to the reaction, the latter not.

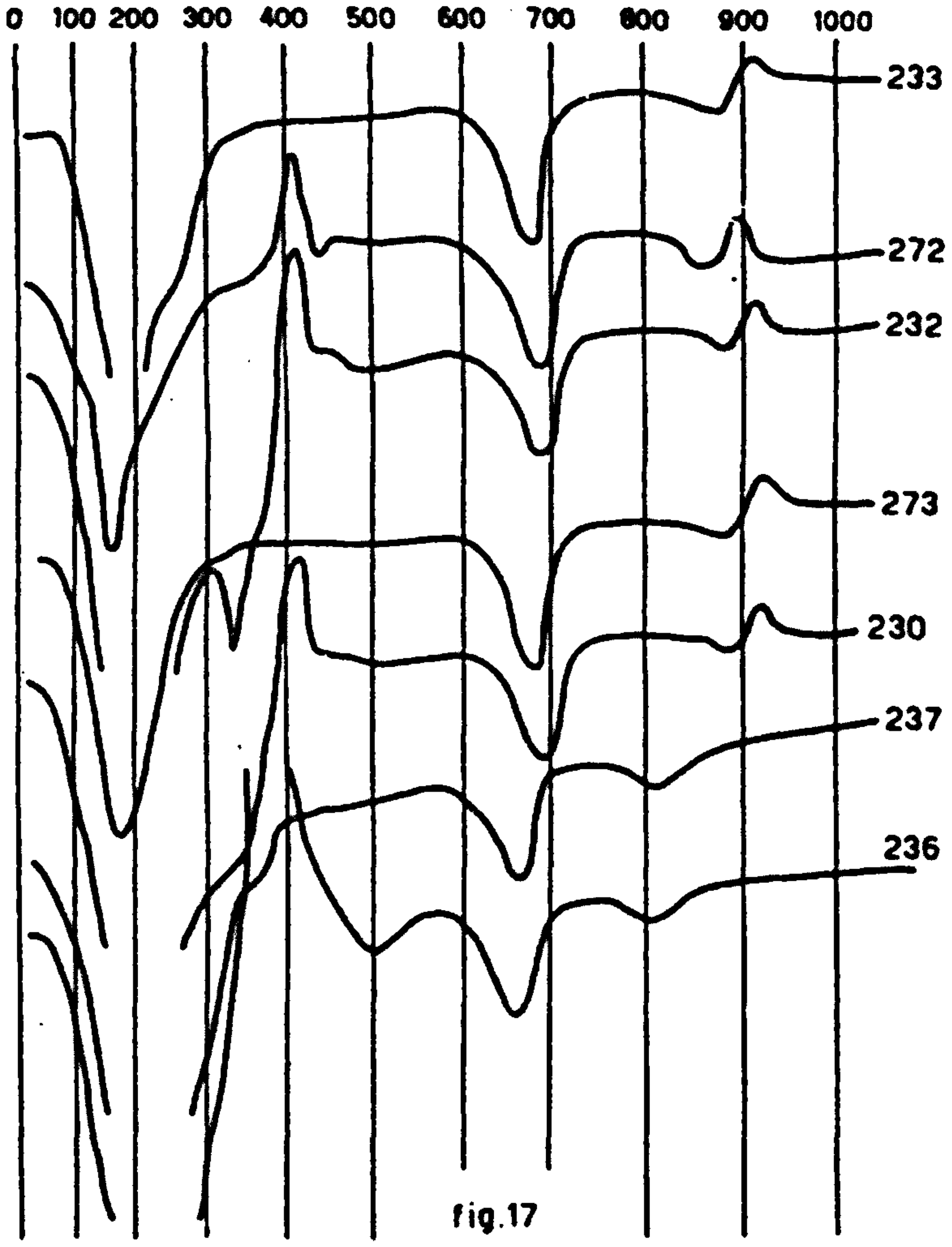


fig.17

DTA curves of montmorillonites, glycerol treated and methylated. Run no. 233: montm. from Wyo. bentonite. 272. the same, methylated, 232. the same glycerol treated. 273 Geisenheim, natural, 230. the same, glycerol treated. 237. Thixoton, 236, the same, glycerol treated.

Conclusions.

Summarizing this paragraph, the following may be said:

1. Salt admixtures in the clay may seriously interfere with the appearance of reactions in DTA, but not if present in quantities smaller than about 2%.
2. By means of various treatments with organic materials (glycerol-solvation, methylation), the identification of the clay-minerals of the montmorillonite group may be facilitated.

§ 15. Summary of the relative importance of the factors. Final remarks.

With the data at hand, and those of others, briefly reviewed in this chapter, it is clear that there are various ways in which DTA curves may be modified. Some of the modifications may improve the records of certain reactions, while at the same time other reactions may be seriously inhibited. In order to avoid mistakes and to get maximum information about a clay under investigation, the operation under different experimental conditions with the same sample, is fully recommendable.

The conclusions from the various paragraphs in this chapter is given in tabulated form in table 7. The relative importance of the factors involved is indicated by plus and minus signs.

Table 7.

Summary of the relative influence of various experimental factors upon the DTA records of clays.

Factor	modifies: peak shifting	peak height	peak range	peak surface
heating rate	++	++	++	++
Ni sample block	-	+	+	+
Ceram. sample block	-	+	+	+
increasing radius of holes	++	++	++	+
increasing depth of holes	++	++	++	+
thermocouples	---	-	-	-
nature of inert substance	++	-	-	-
tight packing	-	+	-	+
covering the holes	++	++	++	++
increasing vapour pressure	++	++	++	++

The practicability of DTA thus greatly depends upon experimental conditions. When starting with DTA the thing is to find out the best operating conditions, in order to get the most valuable records. In this study it was found impossible to give a single formula for these best operating conditions, though certain recommendations can be made.

Steep heating rates and tight packing were found to be desirable. The heating rate of 10 - 12 degrees C per minute, usually recommended in the literature (174, 271), was found insufficient in most cases. The heating rate should be 20 degrees C per minute or higher, as steep heating rates enhance all types of reaction. Tight packing also tends to accentuate all types of reaction.

As regards the other experimental factors, no generalizations could be made. A nickel sample block has no general advantages over a ceramic block, as in the former the exothermic reactions tend to be accentuated and in the latter the endothermic reactions are enhanced. Deep and narrow sample holes in the holder have no general advantages over wide and shallow holes; the reactions accompanied by weight loss are accentuated in the former type of holes, while oxydation reactions and exothermic inversion reactions are accentuated in the latter type.

Likewise, variation of the inert substance and the use of calcined clay as such, has advantages in certain respects and disadvantages in other respects, depending on the nature of clay to be investigated.

However, this variability of experimental conditions is one of the main advantages of DTA over other methods of clay minerals identification; By a choice of optimum operating conditions it enables one for any particular case to get the maximum information available. In other words: the operating conditions should be adapted to the problem to be studied.

If one is to study qualitatively the nature of clay the following guide lines can be set down:

1. kaolinite materials, including halloysites, can be identified succesfully under the following operating conditions:
    - a the heating rate should be moderate to steep (10 degrees C per minute or higher);
    - b a nickel block or other block with great heat conductivity coëfficient should be used;
    - c the ratio of depth to radius of the sample holes should be 1 or greater than 1;
    - d the packing should be tight;
    - e covering of the sample holes during the run may be advantageous;
    - f there is no preference as to the inert substance to be used.
2. If illite materials are expected to be present, the following recommendations can be made as to operating conditions:

- a a steep heating rate (20 degrees C per minute or higher);
- b the use of a ceramic block or other block with low heat conductivity coëfficient;
- c a narrow, and deep sample holes;
- d packing in the holes should be tight;
- e calcined clay should not be used as inert material, but preferably calcined Al_2O_3, to detect admixtures of quartz;
- f covering of the holes is not recommendable, as then the oxydation of ferrous iron, which may be present in the lattice, is masked (as in glauconite for instance).

3. If montmorillonitic clay-minerals (and vermiculites) are expected to be present, the same operating conditions as were indicated for illitic materials can be recommended, except 2^c. Often the use of sample holes with a ratio of depth to radius of 1 or more is advantageous for montmorillonites, in order to detect the high temperature inversion reactions.

4. For the detection of hydrous oxydes of iron and alumina (if present in small quantities) the following operating conditions may be recommended:
   - a a steep heating rate (20 degrees C per minute or higher);
   - b two subsequent runnings should be made, one in a block with great heat conductivity coefficient and one in a block with small heat conductivity coefficient, to be sure that no endothermic reaction is overlooked;
   - c the ratio of depth to radius of the sample holes should be 1 or greater than 1;
   - d packing should be tight;
   - e there is no preference as to the inert substance to be used;
   - f covering of the sample holes is advantageous.

5. Carbonates can be detected with ease under various conditions, but the following recommendations may aid:
   - a a moderate to steep heating rate should be preferred;
   - b the use of a ceramic sample block is adviseable;

c the ratio of depth to radius of the sample holes should exceed 1 for calcite, dolomite, aragonite, smithsonite and other non-oxydiseable carbonates; the ratio should be about 1 for siderite, rhodochrosite and other carbonates subject to oxydation;

d generally the sample holes should not be covered during the running.

CHAPTER IV

THEORETICAL CONSIDERATIONS OF THE DIFFERENTIAL THERMAL ANALYSIS

As has been seen in the preceding chapters, DTA of clay consists of the recording of thermal reactions, produced during heating. The recording is made by means of a differential thermocouple with one junction inserted in the clay sample. The reference junction is inserted in any thermally inert substance. Both substances are heated simultaneously in the same furnace.

For an adequate understanding of the records and for an explanation of the peculiarities, indicated in chapter 3, it is neccessary first to consider the heat mechanics in the samples and in the sample holder. This includes an understanding of the effect of heating rate, depth and radius of the sample holes, thermal properties of clay and inert substance, etc..

Furthermore, the kinetics of the reactions in the thermally active substance should be considered, because the reaction rate (expressed as heat of reaction as a function of time) determines the shape of the DTA curves.

§ 1. Theory of heat transfer as applied to DTA.

The clay and the inert sample in one and the same experiment differ among themselves in

a. specific heat;

b. heat conductivity.

Let us first consider the influence of heating upon the mean temperature of the clay sample and the inert sample, leaving out of consideration, for the time being, the difference in heat conductivity.

If the specific heat of the inert material and of the clay resp. amounts c_1 and c_2, it follows for the simultaneous heating of both substances:

for the inert sample $$c_1 = \frac{Q}{m_1(T_2-T_1)} \qquad (1)$$

for the clay sample $$c_2 = \frac{Q}{m_2(T'_2-T_1)} \qquad (2)$$

where Q = number of calories supplied; Q is equal for both samples in one and the same furnace;

m_1 = weight of the inert sample;

m_2 = weight of the clay sample;

T_1 = initial mean temperature of the samples;

T_2 resp. T'_2 = final mean temperature of the samples.

Combination of (1) and (2) gives:

$$c_1 m_1 (T_2 - T_1) = c_2 m_2 (T'_2 - T_1)$$

In order to get straight zero lines over temperature ranges, where no reactions occur the following condition must be satisfied

$$T_2 - T_1 = T'_2 - T_1 ,$$

This condition is only obeyed when

$$c_1 m_1 = c_2 m_2 \qquad (3)$$

In words: the weights of the samples should be inversely proportional to their specific heats (cf. JEFFRIES, 158).

As appears from the literature the condition expressed in equation 3 ordinarily is not satisfied in DTA experiments. This is one of the causes of deviation of the differential temperature line in temperature ranges where no reactions occur.

In the above mention was made of the mean temperature of both clay and inert sample. Actually, no mean temperatures are measured, but real temperatures at time <u>t</u> and distance <u>r</u> from the wall of the cylindrical sample hole. Consequently, the heat conductivity and the dimensions of the sample holes should be considered.

In the following discusssions the thermocouples are assumed to be negligibly small with respect to the mass of clay and inert material present.

The heat conductivity λ of any substance is defined by

$$dQ = \lambda F \frac{dT}{dx} . dt \qquad (4)$$

where Q = the number of calories passing in the time <u>t</u> through a face of area F.

$\frac{dT}{dx}$ = temperature gradient, perpendicular to the face.

For mono-dimensional heat flow it follows from equation 4 for the non-stationary heating proces (see 157, 175, 191[a])

$$\frac{dT}{dt} = a \left(\frac{d^2T}{dx^2}\right) \qquad (5$$

Equation 5 describes the temperature-course in any substance as a function of time t, distance x from the source of heat and the thermal diffusivity a. The thermal diffusivity a is given by

$$a = \frac{\lambda}{c\rho} \tag{6}$$

where c is the specific heat and ρ the specific weight of the material.

For the derivation of equation (5) the reader is referred to the text-books on heat transfer, as for instance, MACADAMS 175, JAKOB 157, KRONIG 190, etc.

The general equation for three dimensional heat transfer in a non-stationary process is

$$\frac{dT}{dt} = a \left(\frac{d^2T}{dx^2} + \frac{d^2T}{dy^2} + \frac{d^2T}{dz^2} \right)$$

where x, y and z represent the three coördinates.

For the heating and cooling of cylindrical bodies NEWMAN (see 157) derived the equation

$$\frac{dT}{dt} = a \left(\frac{d^2T}{dr^2} + \frac{1}{r}\frac{dT}{dr} + \frac{d^2T}{dh^2} \right) \tag{7}$$

where r = radial coördinate;

h = longitudinal axis coördinate.

The line r = R represents the axis of the cylinder.

In cases where r is small compared with h, the heat transport in axial direction may be neglected to the heat transport in radial direction, equation (7) becoming

$$\frac{dT}{dt} = a \left(\frac{d^2T}{dr^2} + \frac{1}{r}\frac{dT}{dr} \right) \tag{8}$$

By choice of sample holders with $h > r$, equation (8) may be used to describe the temperature course in a cylinder as a function of time and distance. A solution of equation (8) is given in appendix I. As is seen there, the particular solution for DTA experiments is:

$$T_{t,r} - T_o = \frac{1}{4a}\frac{dT}{dt} \cdot r^2 + \frac{dT}{dt}\, t \tag{9}$$

where $T_{t,r}$ = absolute temperature at time t and distance r from the wall of the cylindrical hole, in the inert material;

T_o = initial absolute temperature of the experiment;

$\frac{dT}{dt}$ = temperature rise of the furnace, as measured in the inert substance;

r = radius of the sample hole;

t = time;

a = thermal diffusivity of inert substance.

In temperature ranges where no reactions occur in the clay sample, equation 9 may be applied to both clay sample and inert sample. As applied to the clay sample the formulation becomes:

$$T'_{t,r} - T_o = \frac{1}{4a'} \frac{dT}{dt} r^2 + \frac{dT}{dt} t \qquad (10)$$

Subtraction of (9) from (10) leads to

$$T'_{t,r} - T_{t,r} = \Delta T = \frac{1}{4} \frac{dT}{dt} r^2 \left(\frac{1}{a'} - \frac{1}{a} \right) \qquad (11)$$

This equation represents the relation of ΔT with heating rate, radius of the sample holes and the thermal diffusivities of clay and inert material in DTA experiments. Its bearing upon peak shifting and its quantitative importance will be illustrated in chapter V. It suffices here, to indicate that equation 11 is applicable also in temperature ranges in which reactions occur in the clay sample.

In table 8 values of the coefficients a are given for a number of clays and minerals. The values of a are calculated with the aid of equation (6), from the specific weight the specific heat and the heat conductivity coefficient of the several materials.

If the radius of the sample holes and the heating rate in any experiment is known the value of equation 11 may be calculated. As will be shown in Ch.V the calculated values agree fairly well with the observed values.

In the application of the values of a in table 8 to DTA, a complication arises. In powdered substances air is present between the particles, causing a decrease in heat conductivity coefficient of the powder as compared with the solid substance.

SMITH (269[a]) gave a discussion of the influence of porosity upon the heat conductivity of powdered substances and arrived at the equation:

$$\lambda = \lambda_s P_s + \lambda_a P_a \qquad (12)$$

where λ represents the over-all heat conductivity of the (structureless) powder, λ_s the heat conductivity of the solid component, λ_a the heat conductivity of the air, P_s and P_a resp. the fraction of solid substance and the fraction of air per unit volume. P_a and P_s are dimensionless; $P_a + P_s = 1$.

Table 8.

Values of c, ρ, λ and a for different materials, used in DTA experiments.

substance	ρ gr cm^{-3}	c cal gr^{-1} $^{o}C^{-1}$	$\lambda \cdot 10^{3}$ *) cal cm^{-1} $^{o}C^{-1}$ sec^{-1}	$\frac{1}{a}$ *) sec cm^{-2}
Al_2O_3(calc.)	3.8	0.185	1.62	433
kaolinite	2.68	0.233	0.72	867
montmorillonite	2.61	0.184	0.69	696
illite	2.69	0.226	0.75	811
muscovite	2.78	0.206	0.86	666
halloysite-2	2.67	0.208	0.84	661
quartz, coarse	2.65	0.238	0.93	678
quartz, fine	2.65	0.238	0.50	1262
chalcedon	2.60	0.193	0.86	584
calcite	2.71	0.208	0.50	1128
dolomite	2.85	0.222	0.61	1038
haematite	5.1	0.182	1.41	658
goethite	4.2	0.249	1.06	987
lepidocrocite	4.1	-	-	-
limonite	3.8	-	-	-
diaspore	3.7	0.180	1.49	447
gibbsite	2.4	0.242	-	-

*) values at room temperature.

Data compiled from: BAVER (20), BLANCK (Hb), HODGMAN (142), JEFFRIES (158), LANDOLT-BORNSTEIN (Tab.), LANGE (180), PERRY(Hb), SINGER (269), SMITH (269^{a}); SOSMAN (273) and de WIT and ARENS (283).

For tight packed powders P_a approximates 0.3, P_s 0.7. The heat conductivity of the air λ is 5,7 . 10^{-5} cal cm^{-1} sec^{-1} $^{o}C^{-1}$ at room temperature. For granitic material λ_s is about 7. 10^{-3} cal cm^{-1} sec^{-1} $^{o}C^{-1}$ at room temperature. The over-all heat conductivity of the granitic powder should equal:

$$\lambda = 0,3 \,.\, 5,7 \,.\, 10^{-5} + 0,7 \,.\, 7 \,.\, 10^{-3} = 4,92 \,.\, 10^{-3}$$

As was pointed out by SMITH the values thus calculated agreed well with the observed values.

In table 8 λ_s is given. For the application of equation 11 however the corrected values of λ should be used, as calculated from equation 12.

In this study P_a and P_s were determined for some tightly packed and very loosely packed clay materials and inert material (calcined Al_2O_3). The values are given in table 9. P_s was calculated from the weight of solid material (m), its specific weight (ρ) and the total volume of the clay in the sample hole ($\pi r^2 h$), according to the equation

$$P_s = \rho_m / \pi r^2 h$$

P_a was computed from P_s, according to $P_a = 1 - P_s$

Table 9.

Values of P_a and P_s for tight packing and very loose packing of some materials used in DTA.

substance	packing	m grms	ρ gr.cm^{-3}	$\pi r^2 h$ cm^3	P_s	P_a
Al_2O_3	tight	0.860	3.8	0.282	0.81	0.19
do	loose	0.410	3.8	0.254	0.42	0.58
kaolinite Banka	tight	0.475	2.6	0.254	0.72	0.28
do	loose	0.365	2.6	0.313	0.45	0.55
montmorillonite,	tight	0.560	2.7	0.282	0.74	0.26
Wyoming	loose	0.330	2.7	0.313	0.39	0.61
illite, Fithian	tight	0.605	2.6	0.313	0.75	0.25
do	loose	0.265	2.6	0.254	0.39	0.61

§ 2. The kinetics of some reactions recorded in DTA experiments.

Most reactions involved in DTA records belong to one of the following types

(1) loss of adsorbed water	Clay $H_2O \rightarrow$ Clay + $H_2O - \Delta H$ cal
(2) loss of lattice water	$R(OH)_2 \rightarrow RO + H_2O - \Delta H$ cal
(3) loss of carbon dioxide	$RCO_3 \rightarrow RO + CO_2 - \Delta H$ cal
(4) oxidation reactions	$4RO + O_2 \rightarrow 2R_2O_3 + \Delta H$ cal
(5) inversion reactions	$R_I \rightarrow R_{II} \pm \Delta H$ cal.

The reactions 1 - 4 are reactions in heterogeneous systems. NERNST and others (see 175^{a}) have pointed out that such reactions are controlled by the rate of diffusion of the escaping or of the entering gas. As diffusion is a process of the first order, it is to be expected that the observed velocity of reaction obeys the equation of first order kinetics, i.e.

$$\frac{dx}{dt} = k\ (m - x) \tag{13}$$

where x represents the quantity of material which reacted up to the time under consideration, m the total quantity initially present, k the reaction constant and t the time.

The reactions of type 5 usually are not of the first order, as has been proved for the $\alpha \rightarrow \beta$ quartz inversion (273).

ZIMMERMAN (283) has discussed the limitations of the application of diffusion control upon heterogeneous reactions. For most reactions involved in DTA (type 1 - 4), however, equation 13 may be used.

MURRAY and WHITE (214) confirmed experimentally that the dehydration reactions of kaolinite, halloysite and montmorillonite might be described as unimolecular reactions, obeying equation 13. These workers made a number of dehydration experiments at constant temperature. If the logarithm of loss-in-weight was plotted against time, straight lines were obtained, as is to be expected from equation 13 in its integrated form

$$\ln \frac{m - x}{m} = - kt \tag{14}$$

The same considerations may be applied to the earlier dehydration experiments of HOULDSWORTH and COBB, and PIETERS.

However, a complication arises in the process of DTA. The reaction constant k in equation 13 and 14 is strongly dependent upon temperature, as is expressed by the ARRHENIUS - van 't HOFF equation

$$k = A\ e^{-\frac{E}{RT}} \tag{15}$$

where E represents the energy of activation, R the gas constant, T the absolute temperature and A a constant with the dimension sec^{-1}.

In the experiments of HOULDSWORTH, PIETERS and MURRAY and WHITE, quoted above, the temperature during dehydration was kept constant. Consequently k was a constant. In DTA experiments however, the temperature during any reaction is not constant, but is increasing. This implies an increase of the reaction

constant k during heating.
For this case, equation 15 may be written

$$\ln k = -\frac{E}{RT} + b$$

where b stands for ln A. Now, since the value of $\frac{E}{R}$ is a constant for any reaction, we may write

$$\ln k = -\frac{\alpha}{T} + b$$

The temperature T in any DTA experiment is a function of the time and the heating rate C, as follows

$$T = Ct + T_o$$

Equation 13 now becomes after substitution of k and T

$$\frac{dx}{m-x} = e^{-\frac{\alpha}{Ct + T_o} + b} dt$$

$$\ln \frac{m}{m-x} = e^b \int_0^t e^{-\frac{\alpha}{Ct+T_o}} dt \qquad (16)$$

Putting $\frac{\alpha}{Ct+T_o} = \frac{1}{u}$ we get, since $t = (\alpha u - T_o)/C$,

$$\ln \frac{m}{m-x} = \frac{\alpha e^b}{C} \int_{T_o/\alpha}^{(Ct+T_o)/\alpha} e^{-\frac{1}{u}} du.$$

$$= \frac{\alpha e^b}{2.303 C} \int_{\frac{2.303 T_o}{\alpha}}^{\frac{2.303(Ct+T_o)}{\alpha}} 10^{-\frac{1}{u}} du.$$

or, solving for x,

$$x = m(1-\exp -\frac{\alpha e^b}{2.303C} \int_{\frac{2.303 T_o}{\alpha}}^{\frac{2.303(Ct+T_o)}{\alpha}} 10^{-\frac{1}{u}} du) \qquad (17)$$

If the experimental conditions C and To and the constants of the reaction $\alpha = Q/2.303R$ and b are known, values of x may be computed for any time t in the experiment. Tables for the integral

$$H(r) = \int_{r_1}^{r_2} 10^{-\frac{1}{u}} du$$

are given by SHERMAN (Ind.Eng.Chem.28:1027 (1936)) for values of r = 0.05 to r = 0.175 and by JAHNKE and EMDE for higher values of r.

In order to avoid the difficulties with the handling of equation 17, it is better to use the equation of the reaction isochore of van 't HOFF. This equation describes the relation of the equilibrium constant K as a function of temperature and the heat of reaction Q

$$\frac{d \ln K}{dT} = \frac{Q}{RT^2} \tag{18}$$

Equation 18 is essentially the same as equation 15. However, K and Q in equation 18 are better accessible than k and E in equation 15.

The way of applying equation 18 to actual reactions was given by NERNST (216^a) when he formulated the third law of thermodynamics.

NERNST states that the heat of reaction Q depends upon the temperature at which the reaction takes place. The relation may be expressed as follows

$$Q_T = Q_0 + \alpha T + \beta T^2 + \gamma T^3 + \ldots . \tag{19}$$

where Q_0 represents the heat of reaction near the absolute zero point of the temperature scale.

Substitution of equation 19 in 18 and subsequent integration leads to

$$\ln K = -\frac{Q_0}{RT} + \frac{\alpha}{R} \ln T + \frac{\beta}{R} T + \frac{\gamma}{2R} T^2 + \ldots + I \tag{20}$$

where I represents the integration constant. In his book (p. 739-742) NERNST derives for I

$$I = \Sigma \nu \varepsilon \tag{21}$$

where $\Sigma\nu$ is the sum of the molecules resulting from the reaction minus the sum of the molecules entering in the reaction and ε is the so called „chemical constant".

For heterogeneous equilibria (reactions of type 1 - 4) equation 20 likewise holds, but K than represents the equilibrium constant of the heterogeneous system. The difficulty in the application of equation 20 lies in the evaluation of the quantities Q_0, α, β, γ..... The quantities α, β... refer to the temperature dependency of the specific heat of the substance under consideration.

However, for most substances no measurements are available of the specific heat in low and high temperature ranges. So it is neccessary to use some approximations in equation 20.

NERNST (p. 741-742) derives as approximated formula:

$$\ln K = -\frac{Q}{RT} + \Sigma\nu \frac{3.5}{R} \ln T + \frac{\beta}{R} T + \frac{\gamma}{2R} T^2 + \ldots \tag{22}$$

Conversion to decimal logarithms and substitution of R = 1.98 cal leads to

$$\log K = -\frac{Q}{4.571} \cdot \frac{1}{T} + \Sigma\nu\, 1,75 \log T + \frac{\beta}{4.571} T + \frac{\gamma}{9.142} T^2 + \Sigma\nu\varepsilon' \quad (23)$$

The second approximation is the omission of the terms containing β and γ, as these are very small in comparison with the other terms. So the final approximation leads to

$$\log K = -\frac{Q}{4.571} \cdot \frac{1}{T} + \Sigma\nu .\ 1.75 \log T + \Sigma\nu\varepsilon' \quad (24)$$

In reactions where gases originate it is more convenient to use the partial vapour pressures of the reactants, instead of the concentrations in computing K. Equation 24 than converts to

$$\log p = -\frac{Q}{4.571} \cdot \frac{1}{T} + \Sigma\nu .\ 1.75 \log T + \Sigma\nu\varepsilon \quad (25)$$

This equation may prove to be a very useful one, as all quantities are independently accessible. The direct proof of the validity of equation 25 is found in the measurements of the vapour pressure of the volatile component as a function of temperature. Such measurements are available for a number of carbonates (DEBRAY, ZAWADSKI, a.o.) and salts containing water of crystallization (e.g. $Na_2SO_4.10\ H_2O$). PIETERS made accurate measurements of p = f (T) with kaolinites, while the measurements of MURRAY and WHITE likewise are very useful, as we have seen above.

From all these measurements it appears that nearby straight lines are obtained if log p is plotted against 1/T. The term containing log T in equation 25 does not interfere seriously in the high temperature range, so that only very slight deviations from the straight line are seen in the log p - 1/T plots. In fig. 18 log p is plotted against 1/T, computed from the data given by PIETERS.

The observed delay of reactions of type 1 - 4 as recorded in DTA, may be understood now. Because these reactions result from monovariant equilibria, the vapour pressure of the gas-component in the direct surroundings of the clay determines the rate of reaction.

The reaction starts (in types 1 - 3) as soon as the vapour pressure of the volatile component in the sample exceeds the vapour pressure of that component in the furnace atmosphere. After the start, however, the reaction does not expire at once, because its course is inhibited by the gas which is formed. The maximum rate of reaction occurs at the peak temperature. It is assumed that at the peak temperature the vapour pressure of the volatile component equals 1 atmosphere, all the air in the reaction vessel being replaced by the evasive component.

The assumption that at the maximum rate of reaction p equals 1 atm. may be adduced by a small calculation. If 1 gram of kaolinite (13 % H_2O) takes a volume of 0.7 cc in a sample hole, the volume of air enclosed is about 0.3 cc. The volume of the water vapour, vanishing upon the dehydration of the kaolinite sample, equals 0.13 x 22220 / 18 = 160 cc. So it is seen that the volume of the originating water vapour is far in excess over the volume of the air space in the sample hole. Therefore it is justified to assume, that already before the peak temperature is reached, the originating gas fully replaces the air, present in the sample hole.

In the quantitative application of equation 25 to the delay of reactions, as observed in DTA experiments, it seems con-

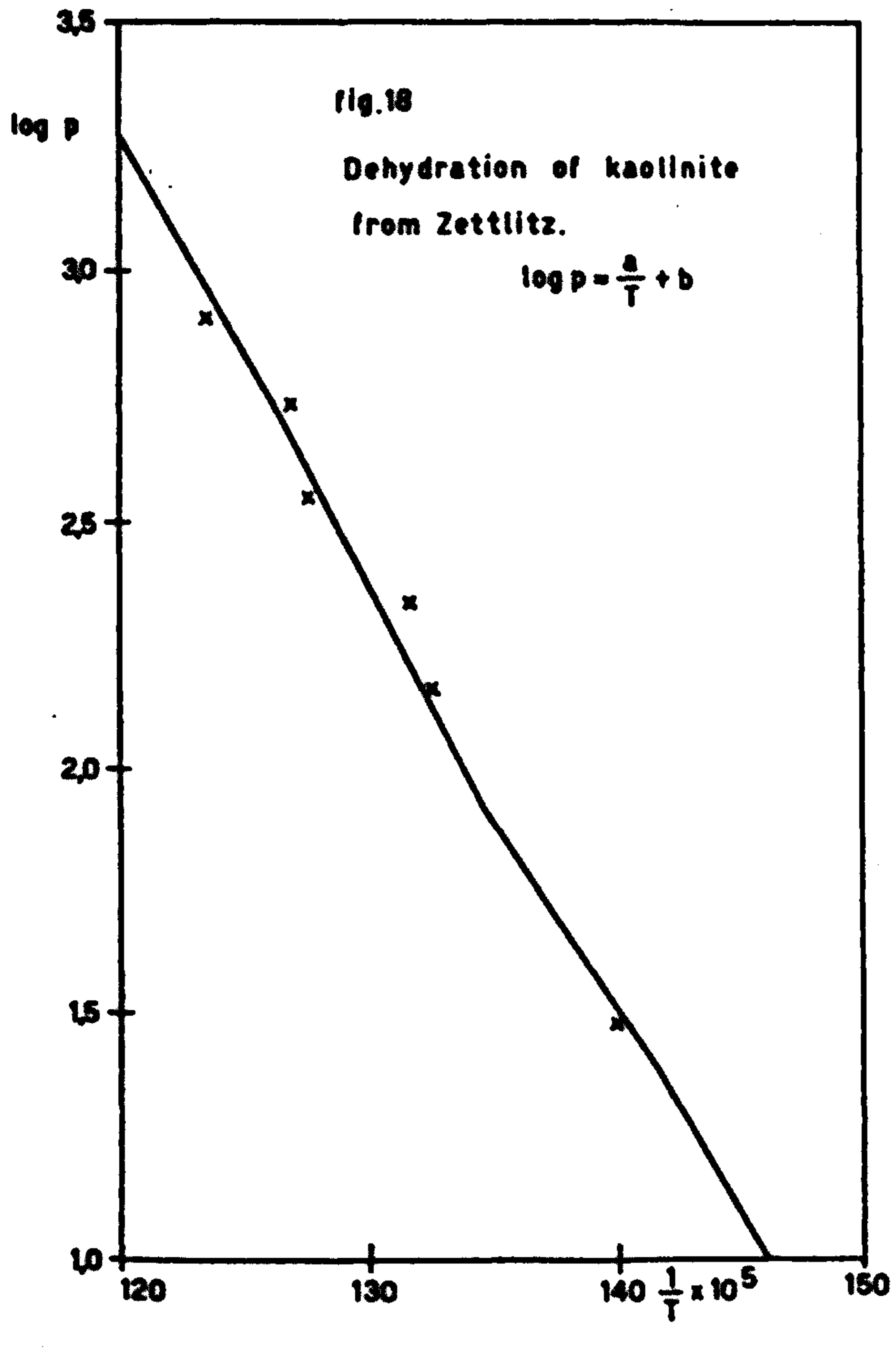


fig.18

Dehydration of kaolinite from Zettlitz.

venient to introduce an asymptotic reaction temperature $\hat{T}$. We define $\hat{T}$ as the absolute temperature at which the reaction starts and finishes in a time approaching infinite, under a heating rate C = o, and under a vapour pressure of the volatile component approaching zero. For a number of reactions $\hat{T}$ is indicated in chapter V, table 12.

The deviation of the real (observed) reaction temperatures from the asymptotic reaction temperatures may be calculated according to equation 25

$$\Delta T = T_{obs} - \hat{T} = \frac{Q}{4.571\ (b-\log p)} - \frac{Q}{4.571\ b}$$

$$= \frac{Q \log p}{4.571\ b\ (b-\log p)} \qquad (26)$$

where b is written for the sum ($\Sigma\nu .\ 1.75 \log T + \Sigma\nu\varepsilon$).

When p is written in mm Hg, the factor b equals:

$$b = \Sigma\nu .\ 1.75 \log T + \Sigma\nu\varepsilon + \log 760 \qquad (27)$$

The value of $\Sigma\nu$ is read from the reaction equation as it represents the sum of the moles resulting from the reaction. Thus for

$$CaCO_3 \longrightarrow CaO + CO_2$$

$\Sigma\nu = 2 - 1 = 1.$

Values of the chemical constant ε are given by NERNST (216^a) for a number of gases and an excerpt of his table is represented here.

Table 10.

Chemical constants for some gases (from NERNST (216^a))

H_2	1.6	CO_2	3.2	NH_3	3.3
O_2	2.8	H_2O	3.6	SO_2	3.3

With the aid of these constants, values of b may be computed with equation 27. It should, however, be born in mind that b is not a true constant, but is dependent of log T. As the variation of log T in the high temperature ranges is only small, b varies only slightly.

In the table 11 some values of Q and b are given for reactions important in DTA of clays.

Table 11.

Values of the heat of reaction Q in cal. per mole and in cal. per gram of some important reactions, and of the factor b.

mineral	reaction	Q cal/mole	Q cal/gr	b calc.	lit. reference
quartz	inversion	180	3	-	Gibson
goethite	dehydration	19000+	220	11.22	-
gibbsite	do	19500+	325	11.23	-
kaolinite	do	77400	300	18.84	Pieters
halloysite	do	69000+	230	18.84	-
illite	do	24000+	60	11.32	-
montmorillonite	do	31000+	90	11.55	-
calcite	loss of CO_2	42500	425	11.03	Debray
aragonite	inversion	390	3.9	-	Foote
siderite	loss of CO_2	19800	170	-	Kelly-Anderson

The values of Q marked with an asterisk + are calculated from thermal data, with the aid of equation 25.

It should however be emphasized that the application of equations 25 and 26 to DTA curves for most minerals is only approximative, as the correct values of Q are lacking. The need for further basic research in this respect is stressed.

§ 3. The qualitative expression of DTA curves; peak shifting.

It was seen in § 1 and 2 that the delay in reactions of type 1 - 3 in DTA experiments has two causes:

1. The gradually increasing partial vapour pressure of the volatile component in the reaction environment, once the reaction has started.
2. The difference in properties, relating to heat transfer, between clay sample and inert sample.

As a summation of these two effects the peak shift amounts to

$$T_{obs} - \hat{T} = \frac{r^2}{4} C \, (1/fa - 1/f'a') + \frac{Q \log p}{4.571 \, b \, (b - \log p)} \quad (28)$$

However, the influence of the nature of the sample holder is not accounted for in equation 28. As is seen from fig. 10 the reaction temperatures are only slightly influenced by the nature of the sample block. The peak area on the contrary is greatly influenced by the kind of sample holder.

Besides the reaction temperatures T_i and T_p, the peak area is another characteristic of DTA curves. In chapter III it was already seen how the peak area is influenced by several factors. Fig. 19 shows how the peak area is influenced by the velocity of temperature rise.

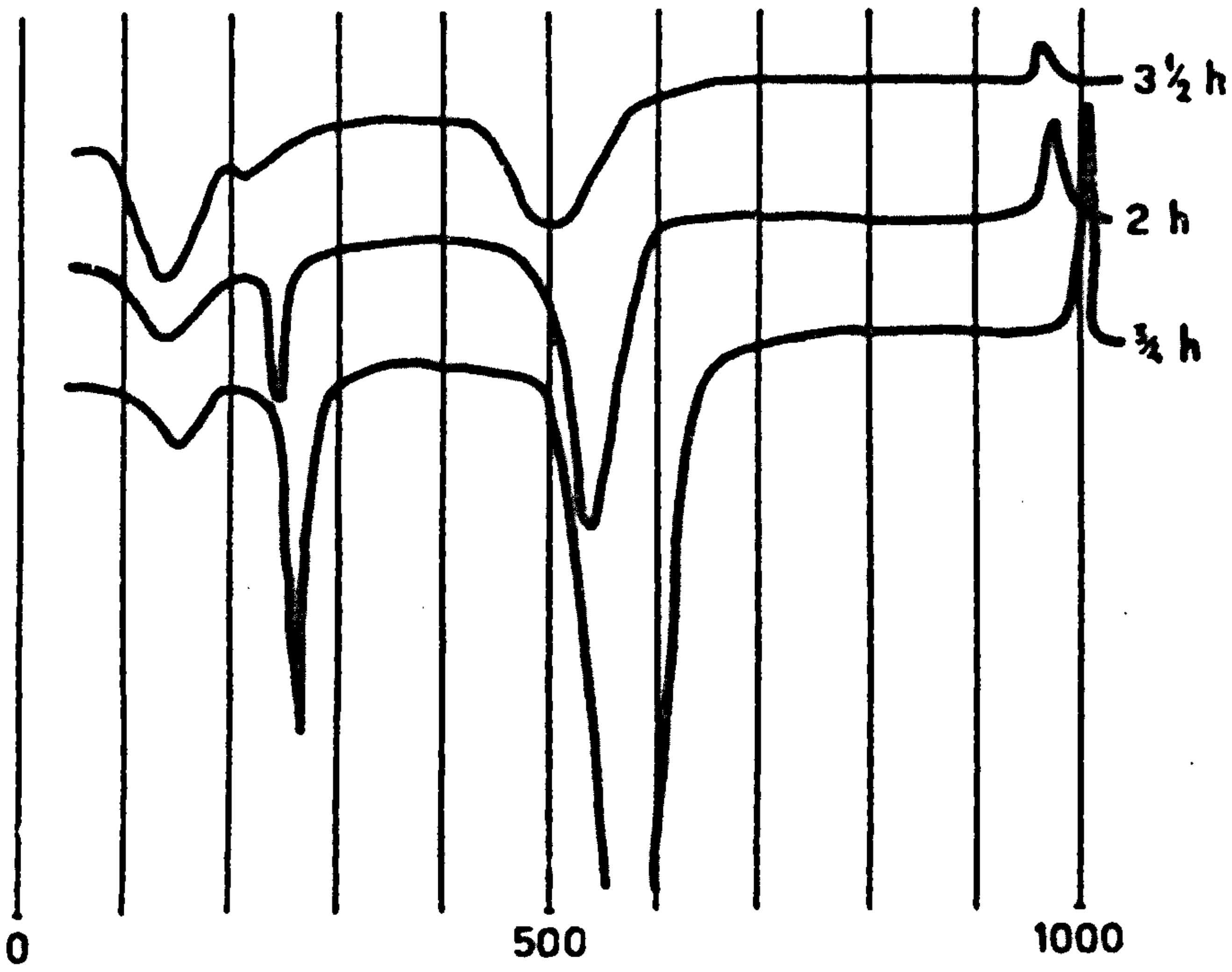


Fig. 19. Influence of the velocity of temperature rise upon the DTA curves of Moengo clay.

The gibbsite present in the clay from Moengo, Surinam, is hardly observeable in experiments with small heating rates, whereas its presence is clearly shown in experiments with large heating rates.

In fig. 10 and in § 3 of chapter III it was shown how the nature of the sample block influences the peak area.

Theoretically the influence of the sample block may be evaluated as follows. If an endothermal reaction occurs in the clay, the heat of reaction must be supplied from the sample block to the reactant. The quantity of heat which is supplied to the samples per unit of time depends upon the temperature gradient in the block and the heat conductivity λ as follows

$$\frac{dQ}{dt} = \lambda F \frac{dT}{dz} \qquad (29)$$

where F is the area under consideration, through which the heat flows.

In ceramic blocks λ is small, in nickel blocks large. The heat supplied per unit of time ($\frac{dQ}{dt}$) is the same in one furnace for all types of blocks, provided the heat capacity of the sample block is negligible with respect to the heat capacity of the active furnace material.

So as equation 29 holds for both ceramic and metal blocks, $\frac{dT}{dz}$ should be larger in the ceramic blocks than in metal blocks. In other words: the records of endothermal reactions are more pronounced in ceramic blocks than nickel blocks.

.In exothermal reactions in the clay sample the heat effect originates in the clay itself. Unlike endothermal reactions, where the heat of reaction is taken up from the block, there is in exothermal reactions an extra quantity of heat originating in the sample. Endothermal reactions thus are delayed with respect to heat supply, while exothermal reactions gain with respect to the heat supply.

Because nickel blocks have a larger heat transfer coefficient than ceramic blocks, the initiation of exothermal reactions is favoured in nickel blocks. Once an exothermal reaction has started, it accelerates itself and thus the time of reaction is smaller in nickel blocks than in ceramic blocks (see fig. 10). Consequently peak heights are greater in metal blocks than in ceramic blocks.

Fig. 20 gives a schematic representation of the course of temperature difference as a function of time and reaction rate.

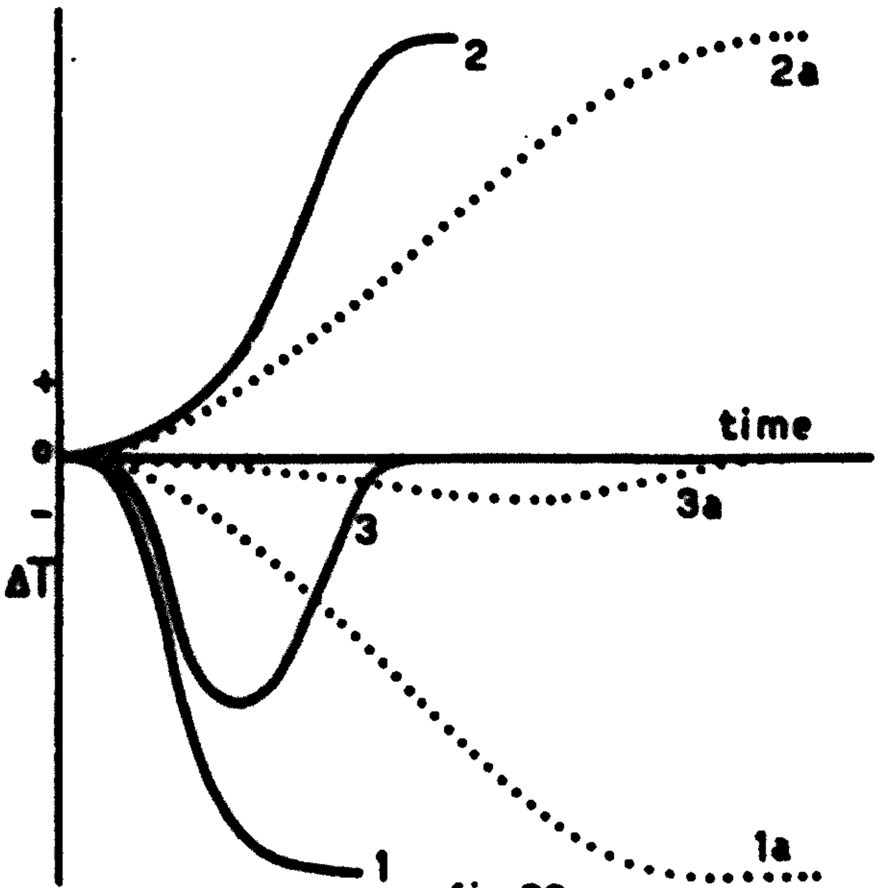


fig.20

The line 1 represents the course of the temperature difference between clay sample and inert sample during an endothermal reaction, for the idealized case, that no heat exchange with the environment should take place during the reaction. In fact, however, such heat supply does take place (line 2), but the temperature course of the heat supply is delayed with respect to the course of the reaction. The net effect is represented by line 3, showing the difference between the values of ΔT of lines 1 and 2 for every value of *t*. Line 3 is the factual DTA curve for an endothermal reaction.

The set of dotted lines represent an endothermal reaction, but here the heating rate of the furnace was assumed to be much smaller. Consequently, the line 2^a is only slightly delayed with respect to 1^a. For a complete understanding of the differential temperature line both gross effects (lines 1 and 2 respectively 1^a and 2^a) should be considered.

§ 4. Some remarks on quantitative with DTA.

The problem in quantitative DTA is to find a relation between any measurable item of the curves and the percentage of the unknown component in a mixture. In chapter 1 § 4 was seen how different authors attacked the problem.

Most workers nowadays (7, 26, 39, 135, 174, 219, 254, 271, 276) consider the area under the peaks as a measure of the quantity of reacting material. So

$$\int \Delta T \, dt = f \, (m) \qquad (30)$$

The various derivations given (a.o. by SPEIL, KULP and KERR, and VOLD), however, are not without defects.

As is seen from fig. 20 the area under the differential temperature peak is equal to the difference of the area under the curves 1 and 2, resp. 1^a and 2^a.

The area under the curves 1 or 1^a may be obtained as follows.

For any reaction, accompanied by a heat effect, one has

$$\Delta T_1 = \frac{Q\,x}{c\,m}$$

where Q is the heat of reaction (per gram), *x* is the quantity of reacting material, and *cm* is the heat capacity of the cell plus contents.

The term *cm* may be considered as the sum of the heat capacities of the various substances, which are raised or lowered in temperature during the reaction

$$c\,m = c_1\,m_1 + c_2\,m_2 + \ldots\ldots \qquad (32)$$

As x in equation 31 is a function of time, according to equation 13 and 16, we may write for the area under curve 1 of fig. 20

$$\int_o^t \Delta T_1\,dt = \int_o^t \frac{Q}{c_1m_1+c_2m_2+\ldots}\,m_1(1-\exp\left[-e^b\int_o^t e^{-\frac{\alpha}{Ct+To}}\,dt\right])\,dt \qquad (33)$$

The area under the curves 2 and 2^a between the time limits t = o and t = t may be represented with close approximation as follows

$$\int_o^t \Delta T_2\,dt = \frac{Q\,m_1}{c_1m_1 + c_2m_2 + \ldots}\int_o^t \tfrac{1}{2}\,dt \qquad (34)$$

The net area of the recorded curve, represented as curve 3 or 3^a in fig. 20 thus is equal to the difference of equations 33 and 34.

$$\int_o^t \Delta T_3\,dt = \tfrac{1}{2}\left(\frac{Q}{c_1} + \frac{Qm_1}{c_2m_2}\right)\left\{t-\int_o^t \exp\left[-e^b\int_o^t \exp\left[-\frac{\alpha}{Ct+T_o}\right]dt\right]dt\right\} \qquad (35)$$

where t is the time of reaction.

Equation 35 shows how the area under the peak depends upon the percentage of reacting material (m_1/m_2), upon the time of reaction and upon the constants of the experiment C and Q.

The time of reaction also depends upon the heating rate C, as follows

$$t = \frac{qm}{(c_1m_1 + c_2m_2 + \ldots)}\;\frac{1}{C}$$

where q is the number of calories, needed to raise the temperature of the cell plus contents from T_i to T_f.

That t is inversely proportional to C was already seen in the values quoted in table 2.

For accurate quantitative analysis with the differential thermal method, the heating rate should be kept the same in the various experiments. The peak area is not independent of the heating rate as SPEIL and coworkers concluded, see fig. 19.

CHAPTER V

THE COMPARISON OF DTA RECORDS OBTAINED WITH DIFFERENT EQUIPMENTS

The general equation for the comparison of reaction temperatures in curves obtained with different DTA equipments is

$$\hat{T} = T_{obs} - \frac{r^2}{4} C\ (1/fa - 1/f'a') - \frac{Q \log p}{4.571\ b\ (b - \log p)} \qquad (36)$$

The units which are employed are

$\hat{T}$ and T_{obs} in ^{o}K or ^{o}C

r in cm

C in $^{o}C\ sec^{-1}$

f dimensionless

a and a' in $cm^2 sec^{-1}$

Q in $cal.mole^{-1}$

p in mm Hg.

The meaning of the symbols is the same as in chapter IV.

In the application to dehydration reactions p represents the partial vapour pressure of water in the reaction vessel at the temperature T_{obs} under consideration. In the application to the decomposition reactions of the carbonates p represents the partial vapour pressure of carbon dioxide in the reaction vessel at T_{obs}. At the peak temperature p equals 760 mm Hg for all reactions accompanied by loss in weight, as was outlined in chapter IV.

In the application to inversion reactions the last term of equation 36 equals zero, as in such reactions no vapour pressures interfere.

In the application of the equation to experiments where the furnace temperature was measured in the centre of the clay sample itself, the term:

$$\frac{r^2}{4} C\ (1/fa - 1/f'a')$$

equals zero, as a = a' in these cases.

The assymptotic reaction temperatures $\hat{T}$ may be obtained in different ways: first of all from very accurate static dehydration experiments, secondly from measurements of the vapour pressure as a function of temperature, and thirdly from NERNST's equation given in chapter IV as equation 25.

In the cases of calcite and kaolinite the three ways of computing $\hat{T}$ lead to sensibly the same results. For other clay minerals there is a considerable lack in our knowledge of $\underline{p}$ as a function of $\underline{T}$, and of the heats of reaction Q. For these minerals $\hat{T}$ may be obtained with some accuracy only from static dehydration experiments.

In table 12 values of $\hat{T}$ for a number of reactions are summarized.

As both the peak temperature (${}_{p}T_{obs}$) and the temperature of initiation (${}_{i}T_{obs}$) of the reactions are considered in the literature, the conversion of both temperatures will be discussed here.

In the application of equation 36 the values of the constants Q and b are taken from table 11, chapter IV.

a. Correction of ${}_{i}T_{obs}$.

The partial vapour pressure of water (p) in the furnace atmosphere determines the value of the last term in equation 36. Unfortunately $\underline{p}$ depends upon the weather conditions prevailing and thus is subject to variation.

In the Netherlands the watersaturation of the air at 18°C is 70% on the average. Hence the partial vapour pressure of water in the air is about 13 mm Hg, and log p equals 1.114. We use this value in our calculations.

As an example we will calculate the correction of ${}_{i}T_{obs}$ for kaolinite. The constants of the reaction are Q = 300 cal/gr = 300x258 cal/mole; b = 18.84.

In a given experiment with kaolinite from Zettlitz values were: r = 0.4 cm; C = 18.5 °C per min. = 0.31 °C per sec.; f = 0.7, f' = 0.8; 1/a = 870, 1/a' = 430 sec cm^{-2}. ${}_{i}T_{obs}$ was 480°C.

If these values are substituted in equation 36 we get:

$$\hat{T} = 480 - 9 - 57 = 414\ {}^{o}C$$

The expected value of $\hat{T}$ was 420 ± 10 °C as follows from table 12. The calculated and the expected value of $\hat{T}$ are in close agreement.

b. Correction of ${}_{p}T_{obs}$.

For the conversion of ${}_{p}T_{obs}$ to $\hat{T}$ equation 36 likewise is used. However p = 760 mm Hg at the peak temperature and log p = 2.881.

In the same experiment as quoted above the ${}_{p}T_{obs}$ was 590°C. Substitution of the constants of the reaction and of the con-

Table 12.

Values of $\hat{T}$ for various reactions of clay minerals, in absolute temperature scale and Celsius temperature scale.

Mineral	Type of reaction	$\hat{T}$		Literature references
		°C	°K	
quartz	inversion	573	846	18, 78, 86, 273
diaspore	dehydration	460	733	224
gibbsite	do	190	463	224
	do	240	513	224
	do	480	753	224
goethite	do	235	508	224
kaolinite	do	420	693	55, 147, 160, 285
	inversion	905	1178	55, 147, 285
halloysite	dehydration	440	713	224
	inversion	905^+	1178^+	-
illite	dehydration	310^+	583^+	224
montmorillonite	do	510^+	783^+	224
beidellite	do	370^+	643^+	224
saponite	do	490^+	763^+	224
nontronite	do	370^+	643^+	224
calcite	loss of CO_2	610	883	77, 80, 224
magnesite	do	400	673	77, 224
dolomite	do	500	773	77, 224
	do	550	823	77, 224

Accuracy for all temperatures $\hat{T} \pm 10^\circ$, except for quartz where the accuracy is $846 \pm 2^\circ$, and for the minerals marked with $^+$ where the accuracy is $\hat{T} \pm 20^\circ$.

stants of the equipment in equation 36 leads to

$$\hat{T} = 590 - 9 - 162 = 418\ ^\circ C.$$

The calculated value of $\hat{T}$ is sensibly the same as the expected value of $420 \pm 10\ ^\circ C$.

c. Application to qualitative analysis.

In a clay soil from Mas d'Auge, S.France, a reaction was noted of rather strong intensity, with the characteristics

$${}_iT_{obs} = 705\ ^\circ C\ ; \quad {}_pT_{obs} = 895\ ^\circ C.$$

The presence of calcite was expected, as the clay reacted strongly with hydrochloric acid. The constants of the experiment were as follows: $r = 0.3$ cm; $C = 11^\circ$ per min $= 0.18^\circ$ per sec.; $f = 0.8$, $f' = 0.8$; $a = 1.44 \cdot 10^{-3}$ (estimated from composition), $a' = 2.326 \cdot 10^{-3}$ cm^2 sec^{-1}.

Under the assumption that calcite was present, Q was taken 42500 cal mole^{-1} and $b = 11.03$.

With these values substituted in equation 36, $\hat{T}$ was found to be equal to

$$\hat{T} = 895 - \frac{0.09}{4}\ 0.18\ (870-530) - \frac{42500.2.881}{4.571\cdot 11.03\cdot 8.15} =$$

$$= 895 - 1.5 - 297 = 597\ ^{o}C.$$

As read from the table $\hat{T}$ of calcite equals 610 ± 10 °C so the assumption that calcite was present in the clay proved to be justified.

d. Conversion of results from different equipments.

A number of runs were made with the same sample of clay, submitted to DTA in different equipments. The results of these experiments, together with the constants of the equipments, are summarized in table 13.

Table 13

Comparative results of some runs in different equipments with identical samples.

Clay sample	run no.	d^{block} mm	h	C	T_i obs °C	T_p obs °C	f	f'
Kaolinite, Banka.	219	3	12	15	440	555	0.8	0.8
	234	6	12	21	455	570	0.9	0.9
	215	7	15	19	455	575	0.6	0.6
	218	8	12	22	460	595	0.5	0.5
	216	8	12	20	455	605	0.5	0.4
	Par$^+$	7	25	11	445	630	0.4	0.4
Illite, Winsum.	82	6	15	7	480	515	0.9	0.9
	11	6	6	17	485	530	0.7	0.7
	130	8	12	13	480	535	0.5	0.5
	Par$^+$	7	25	11	490	570	0.4	0.4
Kaolinite, Ranau.	128	8	12	9	440	565	0.9	0.9
	191	8	12	22	445	595	0.7	0.7
	Par$^+$	7	25	11	440	610	0.4	0.4
Kaolinite, Kaaden.	154	6	6	18	-	565	0.9	0.9
	Par$^+$	7	25	12	-	610	0.4	0.4
Montmorillonite, Wyo.	342	3	12	12	550	675	0.7	0.7
	105	8	12	7	540	665	0.9	0.9
	Par$^+$	7	25	11	600	720	0.4	0.4

$^+$) Runs made by Melle, S.Caillère. Lab.d.Minéralogie, Paris V.

From the T_i and T_p 's given in table 13 the assymptotic reaction temperatures were computed for the cases where <u>a</u> and <u>f</u> were known to a close approximation. The calculated assymptotic reaction temperatures are given in table 14 and compared with the expected values.

It is seen that with the kaolinites the best agreement is found between calculated and expected values of $\hat{T}$.

Table 14.

Comparison of expected and calculated assymptotic reaction temperatures; data from table 13. Relative humidity in Paris 55% at 18°, in Wageningen in most cases 70% at 18°.

Sample	run	Assymptotic reaction temp., °C Calc.from T_p	Calc.from T_i	Expected
Kaolinite, Banka.	219	399	402	420 ± 10
	234	406	413	do
	215	408	414	do
	218	418	410	do
	216	420	415	do
	Par	435	415	do
Illite, Winsum.	82	330	-	320 ± 20
	11	360	-	do
	130	365	-	do
	Par	350	-	do
Kaolinite, Ranau.	128	408	408	420 ± 10
	191	418	412	do
	Par	415	415	do
Kaolinite, Kaaden.	154	407	-	do
	Par	425	-	do
Montmorillonite, Wyo.	342	505	520	510 ± 20
	105	498	512	do
	Par	545	560	do

With illite and montmorillonite the agreement is worse, mainly due to fact that the various thermal constants of the clay (cf. equation 36) were only known as approximations.

CHAPTER VI

SOME APPLICATIONS OF DIFFERENTIAL THERMAL ANALYSIS TO PEDOLOGY

With the recommendations at hand, indicated in chapter III, a number of separate problems have been attacked, the results of which are communicated in the next paragraphs.

§ 1. The application of DTA to clay separates of K-fixating soils.

The minerals, nowadays known for their ability to bind K in a non-exchangeable form, are illites, vermiculites and montmorillonites (15,93,124). The fixation of K in the montmorillonites is known as a slow fixation (243); the fixation in illites and vermiculites as a quick fixation. Both types of fixation are enhanced by alternate wetting and drying, but to a different extent. The fixation in montmorrilonites is the most enhanced by wetting and drying.

However, not all illites exhibit the phenomenon of K-fixation to the same extent. According to Dr H.W.v.d.MAREL *) some illites do not fix at all, while other illites may fix as much as 35 milli-equivalents K per 100 gram of clay (fraction <2 μ). Both the vermiculites and montmorillonites are variable as to their ability to fix K, but do not vary as much as the illites.

From a number of fixating and non-fixating river-clay soils and sea-clay soils of the Netherlands the clay separate (fraction smaller than 2 μ) was analysed. The DTA curves of these clays are reproduced in fig. 21.

The clay from Winsum does not fix K in any appreceable amounts, whereas the clays from Hedel, Veldriel and Etten do (HAUSER, 124). According to DTA and X-ray analysis **) the principal clay mineral in these clays is illite. The differences in the DTA curves of the clays lies in the first endothermic reaction. The non-fixating Winsum clay exhibit only a small reaction at about 150°C. The strongly fixating clays Hedel and Etten exhibit the first reaction much stronger, whereas the curve of the moderate fixating Veldriel lies inbetween.

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*) personal communication.

**) The results of which were kindly reported by Dr H.W.v.d.MAREL

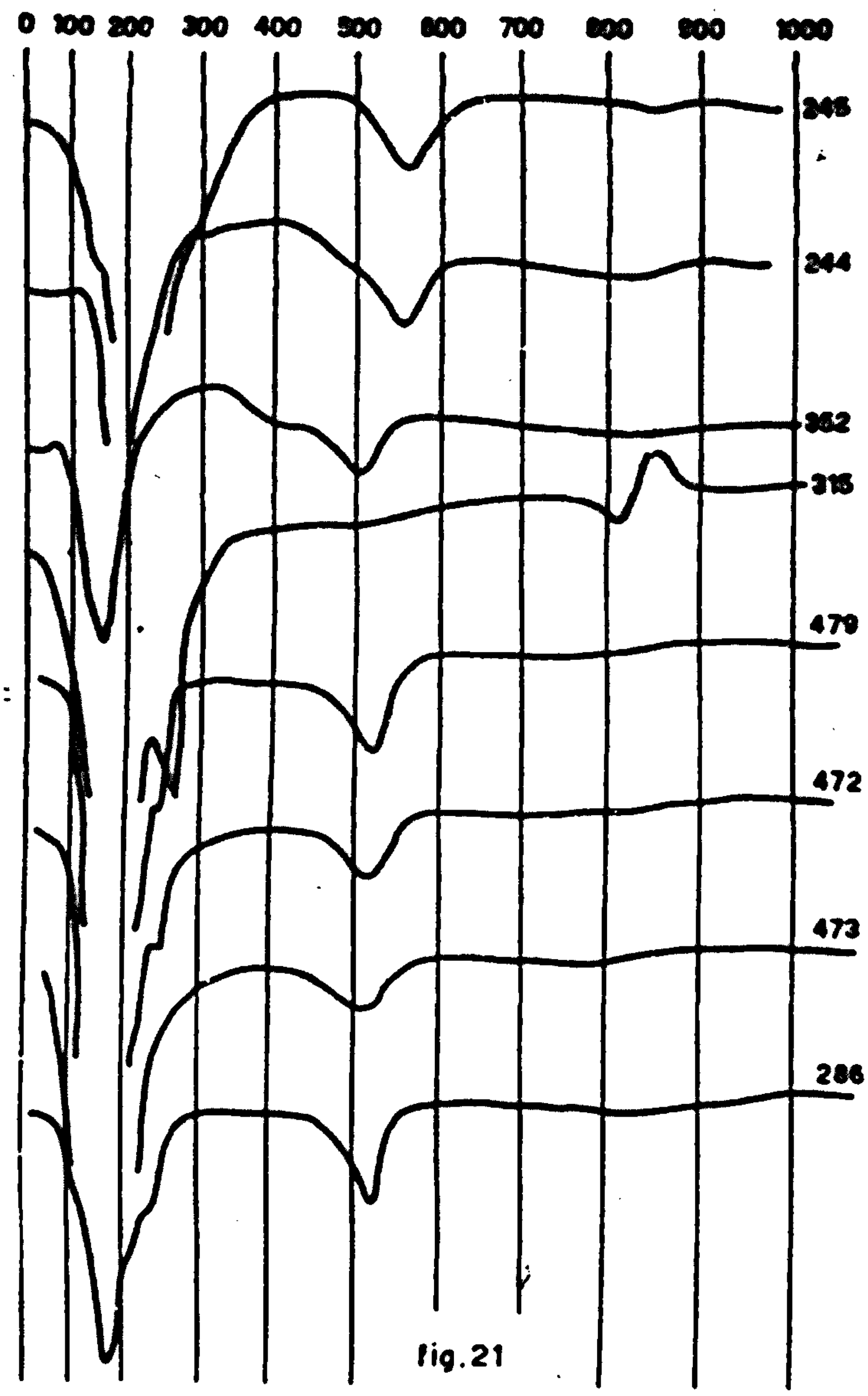

fig.21

DTA curves of some K-fixating clays and clay minerals. 245: Zoeterwoude. 244: Hoge Waard. 352: Kleveneerd. 315: Vermiculite, S.Africa. 479: Etten. 472: Hedel. 473: Veldriel. 286: Illite, Fithian Illinois.

The explanation of an emerged first endothermic reaction in the fixating illites might be found in the lattice constitution of these clay minerals. The crystal structure of the non-fixating illites (which is considered to be almost identical with the structure of muscovite) may be represented by

$$\text{-----}Si_2O_5 \quad . \quad Al(OH)_2 \quad . \quad Si(Al)O_5K\text{-----}$$

The great K-ion is bound electrostatically between subsequent lattice layers. In the case of fixating illites the K is partially absent in the lattice and is isomorphously replaced by any other ion which fixes inbetween the lattice-layers. The most commonly occurring replacement in nature is that by H_3O^+ ions, as was indicated already by TAMM (see HAUSER 124). Additional evidence of the replacement of K^+ by H_3O^+ ions in fixating illites is 1. the greater water content of fixating illites and 2. the more acid reaction of fixating illites, as compared with non-fixating illites.

As the H_3O^+ ions loose water upon heating, at a temperature between 100 and 200°C and the lattice-K do not, it is clear that the first endothermic reaction in the fixating illites is of more pronounced character than in the non-fixating illites. Probably the magnitude of the first endothermic peak is a function of the fixation capacity, but at this time no attempt has been made to prove this statement. The phenomenon of an enhanced first endothermic reaction, however, is obvious for the fixating illites.

A second point of interest with relation to the K-fixation of clay soils is demonstrated in the curves of Zoeterwoude and Hoge Waard (fig. 21). These clays are deposits of the Oude Rijn, an old branch in the delta of the Rhine, and were laid down in Roman times or pre-Roman times. Both clays exhibit rather strong K-fixation. From the DTA curves the clay separates appear to be mixtures of illite and vermiculite. Probably both constituents in these clays are responsible for the fixation.

The presence of vermiculite in clay separates of soils was first found by WALKER (278) in East Ledekin soil and some other Scottish soils, and subsequently by BUEHRER (39) and COLEMAN (57).

§ 2. The presence of mutabilites and metastabilites in soil clays.

In chapter III attention was drawn to the influence of the degree of crystallization upon the thermal reaction temperatures of clays. The presence of clay minerals with different degree of crystallization was first indicated by SEDLETSKII (265). The better the degree of crystallization is, the higher are the reaction temperatures and the more accentuated appear the reactions.

With this statement at hand, the good and poorly crystallized minerals may be distinguished in soil clay. The degree of crystallization of clay, which depends upon environmental conditions (temperature, concentration of the soil solution), probably is not static, but dynamic (JACOB, 155). Under proper conditions the poorly crystallized bodies may convert to better crystallized minerals. Or the good crystallized products may be first dissolved and afterwards precipitated and recrystallized to mutabilites. In relatively high concentrated soil solutions imperfectly crystallized clay minerals may arise, as was pointed out by EDELMAN and SCHUFFELEN (75) and SCHUYLENBORGH (256).

The poorly crystallized clay minerals of the kaolinite-group (the so called fireclay minerals) are distinguished by a relative great amount of adsorbed water, evading from about 100 -200°C (see fig. 22, curve 253, 228 and 223). The water of constitution evades around 550°C, that is at a lower temperature than the well crystallized kaolinites do loose their water. All reactions in the poorly crystallized bodies are relatively faint.

The kaolinite, present in the mottled clay of a laterite profile from Banka (curve 192, fig. 22) appears to be of the poorly crystallized type. This probably accounts for the waterlogging of the mottled clay layer in laterites. Laterites without mottled clay (Ranau, Temangal) only contain well crystallized kaolinites as silicate clay mineral. The well crystallized types hold no adsorbed water; whereas the poorly crystallized types hold adsorbed water in rather great quantities.

Though both clays consist of kaolinites, the physical behaviour of the two soil types is different, on account of the degree of crystallization of the clay mineral.

The curves of well and poorly crystallized hydrous iron oxydes have been given in fig. 14^a chapter III.

Though no factual data are at hand of mutabilites in the illite- and montmorillonite-groups of clay minerals, it is to be expected that with these clays analogous differences occur. Probably any illite is the poorly crystallized form of muscovite in soil clays. The presence of muscovite in the clay fraction of soils was found by FAVEJEE (83, 85).

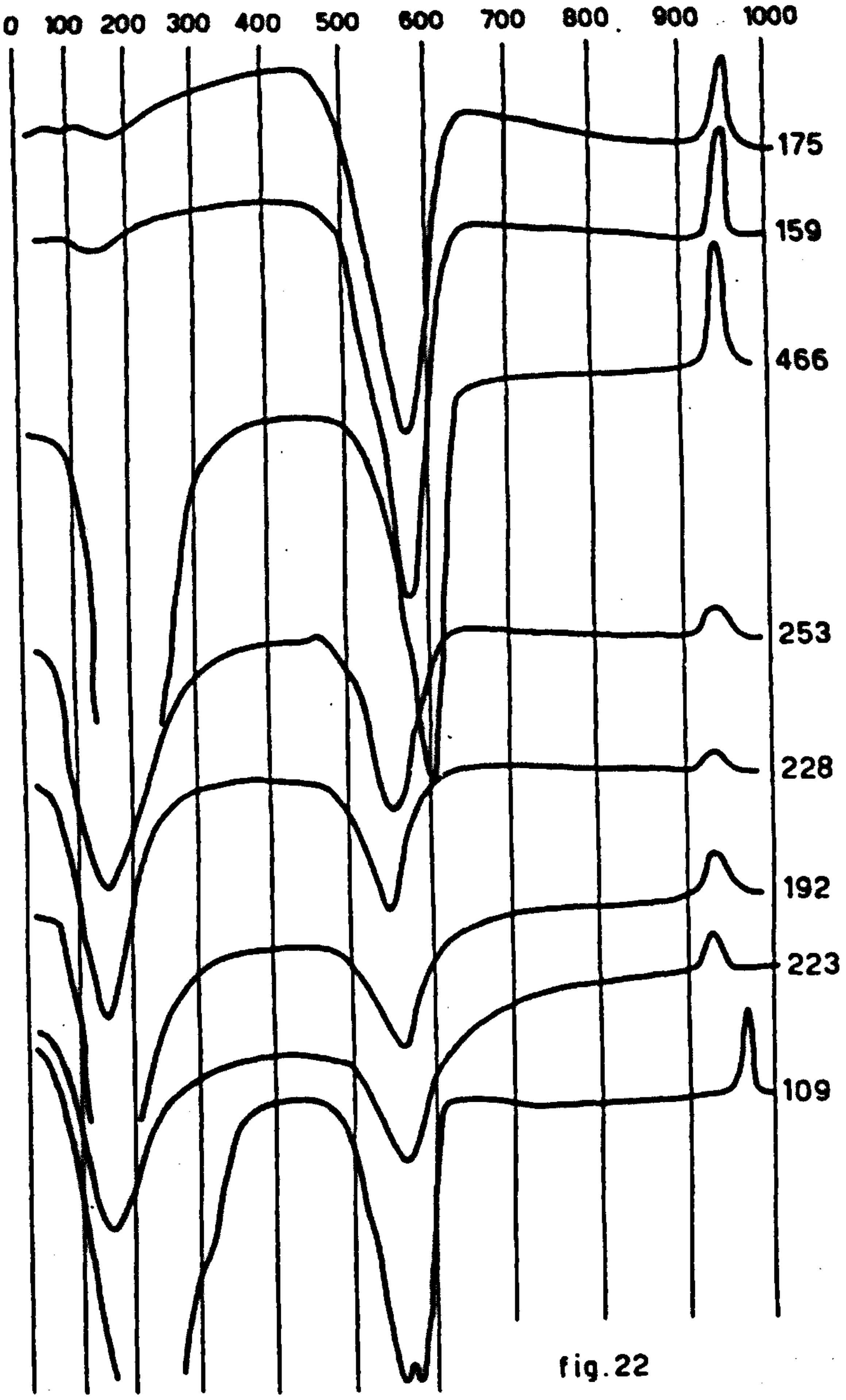

fig.22

DTA curves of some kaolinitic clays and clay minerals. 175: kaolinite Drybranch, Georgia. 159: porcelain earth, Banka, Indonesia. 466: Halloysite, Mindesberg, Germany. 253: bonding clay, Holzhausen, Germany. 228: kaolinite, Meissen, Saxony. 192: mottled clay from laterite profile, Banka. 223: English fire-clay. 109: Djebel Debar, N.Africa.

§ 3. Miscellaneous results.

In fig. 23 a number of curves is represented, related to various tropical and Dutch soils. The Maratakka clay soil of Surinam (curve 310) is a river clay. The clay mineral in this soil appears to be of the illite group, but with some peculiarities. The lattice water evades at about 450°C, being extremely low for illites. According to X-ray records*) the basal spacing of this clay mineral is 7 Å; which is likewise extremely low for illite, and which would rather be an indication of kaolinite. However, the other characteristic kaolinite deflections are absent. Only characteristic illite deflections (except the 7 Å value) are present. Probably it is a new type of clay mineral.

Some other river clay soils of Surinam (curve 285), exhibit the presence of normal illite as a clay mineral in these soils.

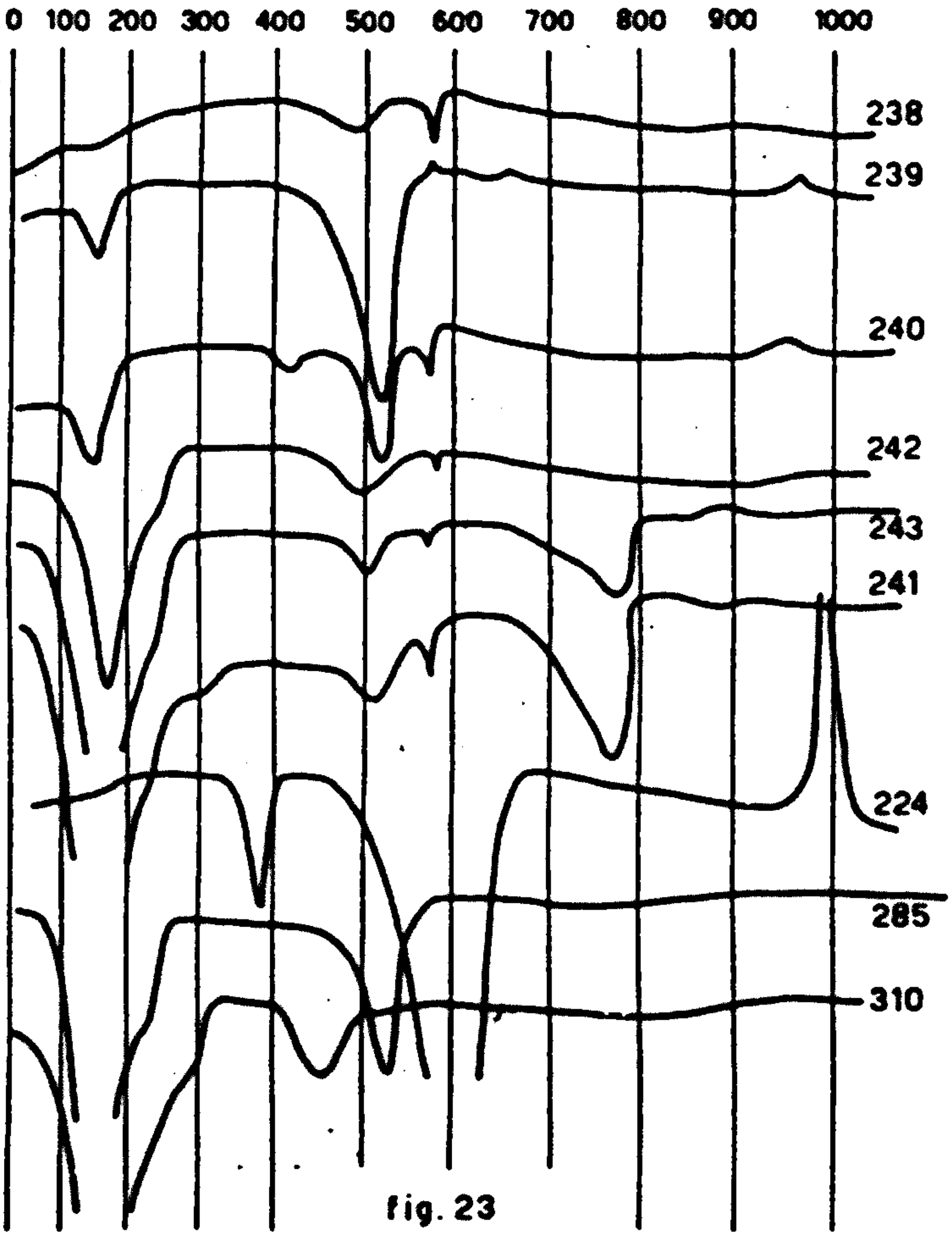

fig. 23

DTA curves of some New Guinea clay soils and of some clay soils from Surinam. 238: Meraukee district. 239: N.Guinea 12. 240: N.Guinea 14. 242: N.Guinea 7. 241 and 243 soils from calcareous parent material. 224: bauxite, Surinam. 285 and 310 Maratakka clay soils (river clays).

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*) personal communication of Dr H.W.van der Marel.

The curves of some New-Guinea soils (No. 238 and 240) show the presence of quartz in great quantities in the clay fraction. In one soil from Sumatra van der MAREL (199) reported likewise the presence of quartz in appreciable quantities in the clay fraction. Further examples of such soils appear to be some of these New-Guinea soils. Such soils, rich in quartz in the clay fraction exhibit extremely bad agricultural characteristics, as bad workability, extremely low water holding capacity and the absence of a sufficient exchange complex.

Some other New-Guinea soils (curves 239, and 242) consist of mixtures of kaolinites and illites or of pure kaolinite. The soils, derived from calcareous parent material contain montmorillonite (curves 241, 243).

Finally a number of curves is reproduced from Dutch soils. Illite appears the most common clay mineral in Dutch soils, as was already found by EDELMAN and FAVEJEE (73), FAVEJEE (81) and van der MAREL (200). The presence of beidellite in clays from calcareous parent material (South Limburg) is indicated in curve 352 (fig. 21).

§ 4. Reaction ranges and reaction intensities of various reactions important in the differential thermal analysis of clays.

In fig. 24 „assymptotic" DTA curves are shown for some of the more important clay minerals. The horizontal axis represents the temperature axis, while the on vertical axis the heat of reaction per one gram of clay is plotted.

Such assymptotic DTA curves may arise theoretically when the conditions are satisfied for the attainment of T, such as were indicated in chapter IV § 2.

From the data which were laid down in table 11 and from the equation 36 in chapter V the actual recorded reaction temperatures may be compared with the assymptotic reaction temperatures.

As was seen in chapter IV, § 4, the peak area is a function of the heat of reaction. It may now be understood, why kaolinites and the hydrous oxydes give rise to well developped peaks, while the illites and montmorillonites exhibit less well developped peaks.

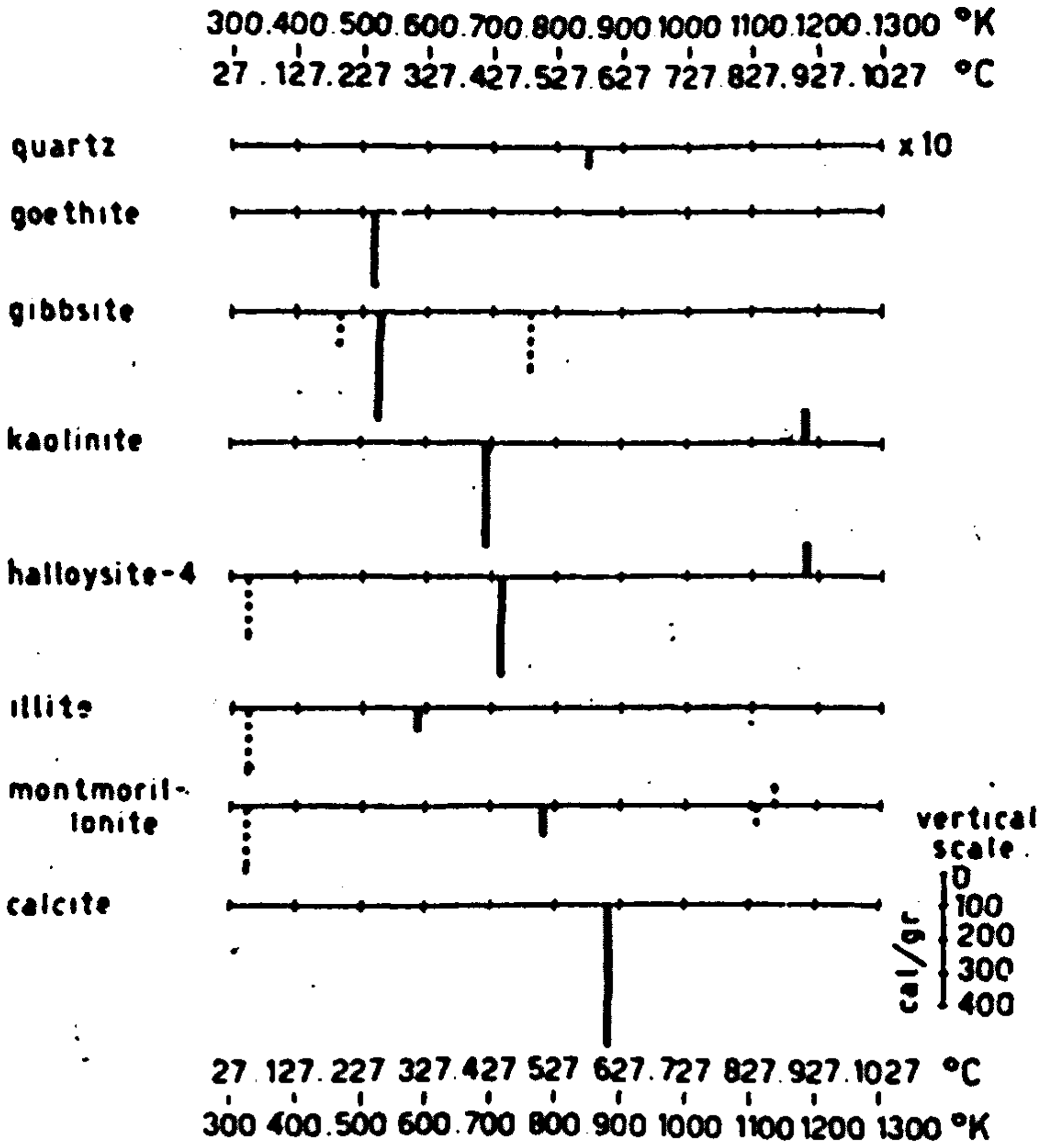

Fig. 24 Assymptotic DTA curves of some clay minerals. The vertical axis represent the heat of reaction in cal/gr. For quartz the vertical scale is magnified 10 times.

SAMENVATTING

Als klei verhit wordt tot hoge temperaturen (1000°C) vinden een aantal reacties plaats. De voornaamste hiervan zijn:

1. verlies van geadsorbeerd water (endotherme reactie);
2. verlies van constitutie water (endotherme reactie);
3. verlies van koolzuur uit carbonaten (endotherme reactie);
4. oxydatie van oxydeerbare bestanddelen (exotherme reactie);
5. rekristallisaties (endo- of exotherme reactie).

Bij de differentiële thermische analyse (DTA) worden de warmte-effecten gepaard aan deze reacties gemeten met behulp van een differentieel thermo-element. Eén loot hiervan bevindt zich in de kleisubstantie, de andere loot in een thermisch inerte stof, b.v. gegloeid Al_2O_3. Klei en inerte stof bevinden zich in eenzelfde monsterblok in een oven. Treedt er geen reactie op in de klei, dan is de temperatuur van klei en inerte stof vrijwel gelijk, zodat het differentiële thermo-element geen e.m.k. bezit. Treedt tijdens de verhitting een endotherme reactie op in de klei, dan uit zich dit in een achterblijven in temperatuur van de klei bij vergelijking met de inerte stof; het differentiële thermo-koppel bezit een e.m.k. Tijdens een exotherme reactie in de klei is de e.m.k. van het differentiële thermo-koppel tegengesteld aan die tijdens een endotherme reactie.

Door nu zowel de oventemperatuur als het temperatuurverschil tussen kleimonster en het inerte materiaal synchroom te registreren ontstaat een DTA curve (zie fig. 9) die voor analyse doeleinden geschikt is.

De ontledingstemperaturen van de verschillende kleimineralen zijn specifiek, zodat hiermee een identificatie mogelijk is.

In principe is DTA de oudste methode voor kleionderzoek in het laboratorium. Zij werd het eerst toegepast door LE CHATELIER. Er bestaat echter een groot aantal tegenstrijdige opvattingen omtrent de interpretatie van de gevonden resultaten.

De voornaamste tegen de methode geopperde bezwaren zijn:

1. het subjectieve karakter van de methode. De resultaten, verkregen met eenzelfde klei, maar onderzocht in verschillende laboratoria, zijn niet identiek. De piektemperaturen kunnen onderling verschillen met een bedrag van 150°;
2. het ontbreken van een theoretische basis, zodat een vergelijking met andere methoden, zoals gewichts analytische dehydratie en thermische dilatometrie, zeer bezwaarlijk is.

Het doel van deze studie is de analyse van het samenstel van factoren, dat de DTA resultaten modificeert.

Na een beschrijving van de gebruikte apparatuur in hoofdstuk II wordt in hoofdstuk III een aantal waarnemingen weergegeven over de factoren die het verloop van de curven bepalen.

Deze factoren kunnen als volgt samgevat worden:

<u>A</u>. factoren gebonden aan de apparatuur:

1. oploopsnelheid van de oventemperatuur;
2. de aard van het gebruikte monsterblok;
3. diepte en straal van de monstergaten in het blok;
4. de plaats van temperatuurmeting van oventemperatuur en differentiële temperatuur;
5. de aard en afmetingen van de thermo-koppels;
6. de aard van de inerte stof;
7. de pakking van de klei en van de inerte stof in de monstergaten;
8. de bedekking van de monstergaten tijdens de analyse;
9. de samenstelling van de damp in de ovenatmosfeer;

<u>B</u>. factoren gebonden aan de klei:

10. de deeltjesgrootte en de aard van de aanwezige kleimineralen;
11. de kristallisatiegraad van de klei;
12. de geadsorbeerde kationen;
13. de aanwezigheid van verontreinigingen in de klei.

Het registratie mechanisme als variabele factor is buiten beschouwing gelaten. Het spreekt vanzelf dat versterking of verzwakking van de thermostromen van het differentieel thermoelement leidt tot een meer of minder geprononceerde curve.

Het blijkt, dat de factoren 1, 3, 6, 8, 9, 10 en 11 de piekverschuiving bepalen, terwijl de factoren 1, 2, 4, 7, 8, 10 - 13 de algemene vorm van de curve bepalen (zie fig. 10 - 12, 14 - 17 en 19). In de tabellen 2, 3 en 5 zijn een aantal quantitatieve gegevens over piekverschuiving, piekhoogte en piekoppervlak vermeld.

Het blijkt dat er vooral twee oorzaken zijn aan te wijzen voor het optreden van de piekverschuivingen, n.l.:

1. Reacties die gepaard gaan met gewichtsveranderingen remmen zichzelf bij een niet-stationnair reactieverloop, doordat de ontledingsproducten niet ogenblikkelijk afgevoerd worden.
2. Zuiver thermische oorzaken, die bepaald worden door het feit, dat zich op ieder moment van temperatuurmeting geen

thermisch evenwicht heeft ingesteld in klei en inerte massa.

In hoofdstuk IV wordt de formulering van beide effecten gegeven; het blijkt dat de piekverschuiving ($T_{obs}-T$) als volgt met de experimentele condities samenhangt:

$$T_{obs} - T = \frac{r^2}{4} \dot{C} \ (1/fa - 1/fa') + \frac{Q \cdot \log p}{4.571\ b\ (b - \log p)} \quad *)$$

De invloed van de warmte-overdrachtscoefficient en van het warmte-geleidingsvermogen van het gebruikte monsterblok is niet in de formulering opgenomen; het effect hiervan op de piekverschuiving is gering, op het piekoppervlak echter groot.

In hoofdstuk V wordt bovenstaande formule toegepast op een aantal waarnemingsresultaten, waaruit de practische bruikbaarheid blijkt. De omrekening van reactie-temperaturen, bepaald met behulp van verschillende apparaten, wordt hierdoor mogelijk.

De toepassing van DTA op enkele speciale problemen uit de bodemkunde wordt gegeven in hoofdstuk VI. Het blijkt dat K-fixerende en niet K-fixerende illieten verschillend reageren (fig. 21): Ook tussen de curven van goed gekristalliseerde kaolinieten en slecht gekristalliseerde kaolinieten bestaan verschillen (fig. 22). De kaoliniet uit de mottled clay laag van laterieten blijkt van het slecht gekristalliseerde type te zijn (z.g.n. fireclay mineraal). In fig. 21 - 23 worden van een aantal gronden uit Nieuw-Guinea, Suriname en Nederland DTA curven gereproduceerd. Enkele N.-Guinese gronden blijken grote hoeveelheden kwarts te bevatten in de kleifractie. De alluviale kleigronden van Suriname bevatten veel illiet; een afwijkend type illiet werd gevonden. De Nederlandse alluviale kleigronden bevatten voornamelijk illiet, wat reeds bekend was uit vroegere onderzoekingen van EDELMAN, VAN BAREN en FAVEJEE. De aanwezigheid van beidelliet in Kleveneerd (Z.Limburg) is waarschijnlijk.

Aan het eind van hoofdstuk VI worden voor enige kleimineralen de assymptotische reactie-temperaturen en de te verwachten reactie-intensiteiten vermeld voor DTA curven. Fig. 24 is getekend naar analogie met de „X-ray data card" voor röntgenanalytisch kleionderzoek. Het gegeven schema is een eerste poging tot een objectieve weergave van de met de DTA gevonden resultaten.

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*) Voor de betekenis van de gebruikte symbolen zie men hoofdstuk IV.

APPENDIX I:

Solution of the differential equation $\frac{dT}{dt} = a(\frac{d^2T}{dr^2} + \frac{1}{r}\frac{dT}{dr})$ as applied to DTA.

The problem is the solution of

$$\frac{dT}{dt} = a(\frac{d^2T}{dr^2} + \frac{1}{r}\frac{dT}{dr}) \qquad (1)$$

I = T as a function of t and r may be represented by the series

$$T_{t,r} = \Psi_0(t) + \Psi_1(t)\frac{r}{1!} + \Psi_2(t)\frac{r^2}{2!} + \ldots + \Psi_n(t)\frac{r^n}{n!} + \Psi_{n+1}(t)\frac{r^{n+1}}{n+1!} + \ldots \qquad (2)$$

where the $\psi(t)$ represent functions of t.
Partial differentiation of T with respect to t in (2) gives:

$$\frac{\partial T}{\partial t} = \Psi'_0 + \Psi'_1\frac{r}{1!} + \Psi'_2\frac{r^2}{2!} + \ldots + \Psi'_n\frac{r^n}{n!} + \Psi'_{n+1}\frac{r^{n+1}}{(n+1)!} + \ldots \qquad (3)$$

Partial differentiation of T with respect to r in (2) gives:

$$\frac{\partial T}{\partial r} = \Psi_1 + \Psi_2\frac{r}{1!} + \Psi_3\frac{r^2}{2!} + \ldots + \Psi_{n+1}\frac{r^n}{n!} + \Psi_{n+2}\frac{r^{n+1}}{(r+1)!} + \ldots \qquad (4)$$

while double differentiation of T with respect to r gives:

$$\frac{\partial^2 T}{\partial r^2} = \Psi_2 + \Psi_3\frac{r}{1!} + \Psi_4\frac{r^2}{2!} + \ldots + \Psi_{n+2}\frac{r^n}{n!} + \Psi_{n+3}\frac{r^{n+1}}{(n+1)!} + \ldots \qquad (5)$$

In order to get the solution of equation (1) we must find the values of the ψ's and ψ''s in the equations (3), (4) and (5).

If equation (3) is to be equal to a times the sum of equation (5) plus $\frac{1}{r}$ times equation (4), the following relation must hold between the coefficients

$$\Psi'_n = a(\Psi_{n+2} + \Psi_{n+2}\frac{1}{n+1}) = a.\Psi_{n+2}(1 + \frac{1}{n+1}) = a.\Psi_{n+2}\frac{n+2}{n+1} \qquad (6)$$

Conversion of (6) gives

$$\Psi_{n+2} = \frac{\Psi'n}{a}\cdot\frac{n+1}{n+2} \qquad (7)$$

With the aid of equation (7) we now are able to express the coefficients $\Psi_0, \Psi_1, \Psi_2, \Psi_3, \ldots \Psi_n \ldots \Psi_{n+m} \ldots$ in the derivatives Ψ'_0 and Ψ'_1; Ψ''_0 and Ψ''_1; ... etc.

So for: n = 0 $\quad \Psi_2 = \frac{\Psi'_0}{a}\cdot\frac{1}{2}$

n = 2 $\quad \Psi_4 = \frac{\Psi'_2}{a}\cdot\frac{3}{4} = \frac{\Psi''_0}{a^2}\cdot\frac{1.3}{2.4}$

n = 1 $\quad \Psi_3 = \frac{\Psi'_1}{a}\cdot\frac{2}{3}$

n = 3 $\quad \Psi_5 = \frac{\Psi'_3}{a}\cdot\frac{4}{5} = \frac{\Psi''_1}{a^2}\cdot\frac{2.4}{3.5}$

... etc.

Substitution of the coefficients ψ in equation (2) leads to

$$T_{t,r} = \psi_o + \frac{1}{a} \cdot \frac{1}{2}\psi_o' \frac{r^2}{2!} + \frac{1}{a^2} \cdot \frac{1.3}{2.4}\psi_o'' \frac{r^4}{4!} + \ldots$$

$$+ \psi_1 \frac{r}{1!} + \frac{1}{a} \cdot \frac{2}{3}\psi_1' \frac{r^3}{3!} + \frac{1}{a^2} \cdot \frac{2.4}{3.5}\psi_1'' \frac{r^5}{5!} + \ldots \qquad (8)$$

In equation (8) the coefficients ψ_o and ψ_1 are functions of <u>t</u> and are given by the conditions of the experiment. In order to determine the ψ's, it is first noted that in well carried out DTA experiments the following conditions should be satisfied.

1. There should be a constant heating rate of the inert material in the sample holder. The condition can be formulated as

$$\left(\frac{dT}{dt}\right)_{r=o} = C \qquad (9)$$

The integrated form of equation (9) is

$$T_{t,r=o} = Ct + T_o$$

where T_o represents the initial (absolute) temperature of the experiment and C the heating rate. To a very close approximation holds as well

$$T_{t,r=R} = C't + T_o \qquad (10)$$

The left hand side of equation (10) represents the temperature of the sample holder as a function of time.

2. All temperatures should be measured on the axis of the cylindrical holes. That is to say, letting T_{obs} represent the observed temperature

$$T_{obs} = T_{r=o} \text{ for all values of } \underline{t} \text{ and } \underline{C};$$

3. The heat is supplied to the samples in the cylindrical holes from all sides. Then the radial temperature gradient in the centre of the holes equals zero for all values of <u>t</u> and <u>C</u>. Thus

$$\left(\frac{\partial T}{\partial r}\right)_{r=o} = 0 \qquad (11)$$

With the aid of these conditions the coefficients ψ_o and ψ_1 may be expressed as functions of <u>t</u>, as follows from equations (9) and (10)

$$\begin{aligned} \psi_o &= Ct + T_o && \text{for } r = R \text{ (and for } r = 0)\ ^{+)} \\ \psi_o' &= C && \text{for } r = R \text{ (and for } r = 0) \qquad (12) \\ \psi_o'' &= 0 && \text{for } r = R \text{ (and for } r = 0) \\ \psi_o''' &= 0 \ldots \text{ etc.} && \text{for } r = R \text{ (and for } a = 0) \end{aligned}$$

+) only when $t \gg \frac{r^2}{4a}$, see below.

and from (11)

$$\begin{aligned} \psi_1 &= 0 \qquad \text{for } r = 0 \\ \psi_1' &= 0 \qquad \text{for } r = 0 \end{aligned} \tag{13}$$

Substitution of the equations (12) and (13) in equation (8) gives

$$T_{t,r} = Ct + T_o + \frac{1}{a} \cdot \frac{1}{2} C \frac{r^2}{2!} + 0 + 0 \ldots$$

$$T_{t,r} = T_o + Ct + \frac{r^2}{4a} C \tag{14}$$

Substitution of equation (9) in (14) leads to

$$\underline{\underline{T_{t,r} - T_o = t\left(\frac{dT}{dt}\right)_{r=o} + \frac{r^2}{4a} \left(\frac{dT}{dt}\right)_{r=o}}} \tag{15}$$

The term $\frac{r^2}{4a}\left(\frac{dT}{dt}\right)_{r=o}$ describes the temperature course within the sample, but only if $\underline{t}$ is large enough with respect to $\frac{r^2}{4a}$. For $\underline{t} \gg \frac{r^2}{4a}$ holds

$$\left(\frac{dT}{dt}\right)_{r=R} = \left(\frac{dT}{dt}\right)_{r=o}, \text{ or } C' = C.$$

Under this condition the temperature difference between the fringe of the sample hole and the centre of the cylindrical sample equals

$$\underline{\underline{T_{r=R} - T_{r=o} = \frac{R^2}{4a} \left(\frac{dT}{dt}\right)_{r=o}}} \tag{16}$$

The question remains as to what is to be understood by the condition $t > r^2/4a$, because this condition determines the applicability of equations (15) and (16). As an aid in answering this question Drs D.A. de VRIES, of the Physical Laboratory, Wageningen kindly drew the writer's attention to the numerical tables in JAKOB's book (157). The table for values of θ/θ_R as a function of time and position of temperature measurement, for the heating of cylinders with $h \gg R$ is represented here.

Table 15

Values of θ/θ_R for the heating of cylinders (with $h \gg R$) as a function of position of measurement of temperature (represented as r/R) for several values of ta/R^2.

	$\frac{t.a}{R^2}$			
r/R	0.08	0.16	0.32	0.80
0	0.016	0.123	0.354	0.691
0.3	0.054	0.191	0.420	0.725
0.5	0.122	0.287	0.505	0.768
0.6	0.268	0.443	0.628	0.828
0.8	0.470	0.621	0.755	0.888
1	1	1	1	1

To test the validity of equations (15) and (16), values of $\frac{\theta_R - \theta_r}{\theta_R}$ have been computed from table 15 and have been calculated according to equation (16). The results are presented in table 16 for comparison.

Table 16

Values of $\frac{\theta_R - \theta_r}{\theta_R}$, computed from table and calculated from equation (16), for several values of r/R and $\frac{t.a}{R^2}$.

$$\frac{\theta_R - \theta_r}{\theta_R}$$

	$\frac{t.a}{R^2} = 0.08$		$\frac{t.a}{R^2} = 0.32$		$\frac{t.a}{R^2} = 0.80$	
r/R	table	calc.	table	calc.	table	calc.
0	0	0	0	0	0	0
0.3	0.038	0.109	0.066	0.072	0.034	0.034
0.5	0.106	0.246	0.151	0.161	0.077	0.077
0.6	0.252	0.436	0.274	0.285	0.137	0.137
0.8	0.454	0.630	0.401	0.413	0.197	0.197
1	0.984	0.984	0.646	0.646	0.309	0.309

It appears from the data in table 16 that only for values $\frac{t.a}{R^2} > 0.32$ the calculation of temperature differences within the cylindrical samples with the aid of equation (16) is justified. Taking the condition as

$$\frac{t.a}{R^2} \geqslant 0.5,$$

equations (15) and (16) are valid for all values of

$$t \geqslant 2 \cdot \frac{R^2}{4a} \qquad (17)$$

Normally condition (17) is fully obeyed in DTA experiments; so equation (16) is valid.

APPENDIX II:

SOME REMARKS ON STANDARISATION OF DTA EQUIPMENT

In view of the bad comparability of DTA curves, resulting from different equipments, the British clay group (MACKENZIE, 191) made some efforts to arrive at a standarisation of equipments.

In chapter III of this study the most important items involved in an eventual standarisation are indicated. It was seen there that quite a number of factors should be covered. In fact, any success of standarisation may be expected only if all equipments, including the recording mechanism, are made as identical as possible. Any proposal to such rigourous reforms can be safely considered unprofitable.

Moreover, in the final section of chapter III was suggested how the constants of the equipment should be chosen in order to get optimal information on any clay submitted to DTA. The identification of illites requires other experimental conditions than the identification of carbonates or of the iron minerals. In view of the different requirements of the various minerals, standarisation probably will prove to be a serious disadvantage.

It was also shown in chapter IV and V how the conversion of data obtained with different equipments may be carried out.

Thus, for qualitative purposes standardisation of equipment is impracticable, disadvantageous and unneccessary.

The only thing which is of interest is the fixation of certain minimum requirements, to which all equipments should respond. The minimum requirements are the following.

1. A continuous and synchronous recording of furnace temperature and difference temperature.
2. The maintenance of a heating rate as constant as possible during any experiment.
3. The measurement of the furnace temperature should be made in the clay sample itself.

The influence of most of the other factors involved and indicated in chapter III may be evaluated with the aid of the formulae given in chapter IV and V.

For quantitative purposes there is no need for standardisation as long as the analysis remains empirically and the minimum requirements, indicated above are fullfilled. What is of interest here is, however, the expression of the deviations of the differential temperature line in terms of calories. When this problem can be solved, a discussion about standardisation will be more fruitful.

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