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LIMESTONE INVESTIGATIONS

THE DEVELOPMENT, OPERATION AND USES OF A DIFFERENTIAL THERMAL ANALYSIS UNIT

by

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ABSTRACT

The setting up of the equipment from its components, the difficulties encountered and the solution of associated problems are described.

Variations in technique which may affect results are considered and the methods used in this laboratory for eliminating these variables are discussed.

Both quantitative and qualitative differential thermal analysis for use in this laboratory are discussed.

1. INTRODUCTION

In differential thermal analysis (abbreviated to d.t.a.), a sample of the material under investigation (the specimen or sample) is placed side-by-side with a sample of a thermally inert material (reference or inert) in a suitable specimen holder and the temperature difference between the two is continuously recorded as they are heated. When a reaction commences the sample becomes hotter or cooler than the inert material and a peak develops on the curve where temperature difference against time $\left(\frac{\Delta T}{t}\right)$ or against temperature $\left(\frac{\Delta T}{T}\right)$ is plotted.

Differential thermal analysis has a wide application - in ceramics, organic and inorganic chemistry, metallurgy and other fields, hence there are many types of apparatus. Results are affected by factors connected with apparatus, technique and the samples investigated.

The main components of the apparatus are the specimen holder and block, the temperature regulating system and the system used for measuring temperature differences between the sample and inert substance.

The principal factors to be considered are heating rate, positioning of thermocouples, size, pre-treatment, packing and dilution of the sample under investigation. The type and particle size of the inert material may also affect results. These factors cumulatively can exert an enormous influence on the curves obtained.

This report includes a discussion on the different types of apparatus which may be used, the various techniques employed and the uses which may be made in this laboratory of a differential thermal analysis unit.

The problems involved in setting up the equipment from the various components is discussed together with the remedy used to overcome them.

2. APPARATUS

2.1 Heat Source

Any controllable heat source may be used. Lewcock and Wylde (1953), used a liquid bath but although other similar arrangements may suffice, electrically-heated furnaces are almost universally used.

In any furnace used, two features are essential:-

(i) There must be sufficient heat output to raise the temperature of the contents at a more rapid rate than desired over the chosen temperature range.

(ii) The specimen holder must be heated evenly. Tube type furnaces can be readily made to satisfy these requirements. Vertically or horizontally mounted models may be used. The model available for use in this laboratory is a horizontal tube-type Gallenkamp furnace wound with nichrome wire. It is possible to attain temperatures up to 1100°C. with this model.

It is extremely important to ensure that induced electromotive forces are not present which may cause A.C. feed-back to the recorders through the thermocouple wires. Considerable difficulty due to this effect was originally encountered with this Gallenkamp furnace at temperatures above 500°C. An earthed sheet of nickel foil placed inside the furnace between the block and the walls was satisfactory but was effective for only three or four experiments because of the rapid oxidation of the foil. The simplest solution to this problem was the use of a stainless steel block which could be earthed.

2.2 Temperature Regulating System

The main essential of furnace-temperature control for accurate and reproducible results is that the rate of temperature increase should be reproducible. It is desirable, but not absolutely necessary that the temperature increase should be uniform. Since reproducibility is required, manual maintenance of the heating rate is not suitable. The only really satisfactory methods are those utilizing the furnace temperature for accurate control to a fixed temperature cycle.

A suitable temperature controller operates on the principle that immediately the furnace is overheated or underheated a lower or higher current or voltage is applied to rectify the conditions. In this manner the control may be made to follow a predetermined cycle very accurately.

The unit used in this laboratory is a high-low voltage type with a motor driven auto-transformer with two contacts set just sufficiently apart for control. The apparatus consists of a Philips programme transmitter type PR7211, which incorporates a rotating drum with a bronze wire attached shaped to the required programming curve. The drum, which has several gear ratios to give various rotation speeeds, is driven by a synchronous motor. A modified Brown Honeywell type M904 Modutrol motor coupled to a Variac and a Philips type PR4062 A07 proportional controller connected to the programme transmitter enables a reproducible and steady heating rate to be maintained. The proportional controller supplied was calibrated for chromel-alumel thermocouples and the full-scale deflection of the instrument has now been modified for the use of platinum-platinum + 10 per cent rhodium thermocouples. The temperature trace is recorded on a chart by a pen attached to a carrier.

2.3 Specimen Holder and Block

All types of apparatus use some sort of specimen holder but no single design can be regarded as standard (Mackenzie 1957). Most conventional types of apparatus have a specimen holder of circular or rectangular cross-section, accomodated in a larger block which may or may not be of the same material.

2.3.1 Block.

The block used in this laboratory is made from stainless steel shaped to fit securely in the furnace. A steatite section fits on two pegs attached to the block and seals the furnace opening. One of these pegs is fitted with a screw to which the earthing wire is attached. A rectangular well ($\frac{3}{4}$ inch by $\frac{3}{4}$ inch by $\frac{1}{2}$ inch) is drilled near one end of the block and two holes drilled longitudinally through the block, housing the thermocouples, meet this well. The block is fitted with a tightly fitting lid.

2.3.2 Sample Holder.

A steatite sample holder shaped to fit in the well, has two cavities approximately 3/16 inch in diameter and ¼ inch depth, in which the sample and inert material are placed. In the original equipment an alundum block and cell were used but because of the difficulties in earthing the alundum, the steel block was substituted.

2.4 Temperature Measuring System

Most investigators use thermocouples for temperature measurement. The choice of thermocouples is governed by certain factors:-

(i) They should not be affected chemically by either the materials or the reaction products.

(ii) They should give an easily measurable electromotive force for the amount of material under investigation.

Rare-metal thermocouples have certain attractions despite their initial cost because they are more robust and generally have a longer life than base-metal couples. Work originally carried out in this laboratory was hindered by continual breakage of chromel-alumel wires. When various mixtures evolved sulphur dioxide on heating the wires had to be rewelded after only two experiments. Since the apparatus required standardizing when new thermocouples were used, considerable loss of time resulted.

Platinum-platinum + 13 per cent rhodium couples were used for some time but the apparatus has now been modified for the use of platinum-platinum + 10 per cent rhodium since this system is most widely used. The wires are of approximately 0.3 millimetre diameter.

It is extremely important to ensure that the thermocouples are welded to give junctions of the same bead size, otherwise thermal gradients may be set up which would cause base-line drift on the differential trace. Positioning of thermocouples is also important for the same reason. However, it is a matter of practice, by trial and error, by the investigator to overcome these difficulties.

The two thermocouples are arranged so that the difference in temperature of the sample and the inert material are registered and the sample temperature is used as the temperature control.

2.5 Differential Recorder

The difference in temperature of the sample and inert material is recorded continuously on a Philips Type 4060 M13 pen and ink recorder.

3. TECHNIQUE

It is extremely difficult to formulate a standard technique which will give reproducible results for any type of reaction studied. Factors affecting results are:-

(i) Particle size of the sample
(ii) Pre-treatment procedures
(iii) Weight of sample,
(iv) Choice of the inert material
(v) Position of the temperature thermocouple
(vi) Heating rate.

It is obvious that a standard technique for the class of reactions studied must be developed by each investigator and constant practice is required to determine the most suitable conditions.

Differential thermal curves, apart from being influenced by differences in apparatus, are particularly sensitive to variations in technique. With this in view Mackenzie and Farquarson 1953 have suggested the following points on technique:-

(i) Irrespective of the type of furnace, a heating rate of 10°C. per minute, with a maximum variation of $\pm 1^{\circ}$ per minute should be aimed at.
(ii) The rate of temperature increase should be uniform.
(iii) In all publications the position of the temperature thermocouple should be stated (i,e. whether in the inert material or in the sample).
(iv) If the temperature thermocouple is in the inert material it should be stated whether the peak temperatures were corrected to the temperature of the specimen;
(v) The greatest accuracy possible should be sought when quoting peak temperatures - preferably $\pm 3^{\circ}$ C.
(vi) The packing of the material in the specimen holder should be uniform, and hard packing is recommended.
(vii) No standard size of sample can be recommended but sample weight should be stated in all publications.

3.1 Positioning of Thermocouples

Considerable difficulty was experienced with base-line drift on the differential trace when alundum sample containers or cells were used. The opening in the side of the cell enabled only the tip of the thermocouple to be inserted in the sample and the inert substance; consequently any slight movement of the apparatus caused the thermocouples to move from a central position thus setting up a temperature gradient between them. This effect caused serious base-line drift as a result of which the estimated peak temperatures and areas were inaccurate.

However, by use of techniques developed by practice, the thermocouples may now be positioned accurately with the beads centrally placed in each compartment. The sheaths around the thermocouple wires fit firmly in the block and provided that reasonable care is taken, are unlikely to allow any movement from the central position.

Positioning of the thermocouples is the first part of the operation.

3.2 Pre-treatment and Weighing of the Sample

3.2.1 Pre-treatment of sample.

The extent of pretreatment of samples in differential thermal analysis depends markedly on the type of sample studied. Mackenzie (1957) has recommended that all samples of clays be stood over a saturated solution of $Mg(NO_3)_2.6H_2O$ for four days in vacuo to attain equilibrium of water vapour.

When similar compounds are under investigation, it is essential that they should all be of approximately the same particle size. This may be achieved by grinding the sample and passing it through a standard mesh screen.

Dilution of the sample is necessary when its thermal characteristics and that of the inert material are very dissimilar. If the sample is not diluted marked base-line drift occurs. When the sample is suitably diluted with the inert substance, the thermal characteristics of each should approximate closely, and base-line drift should be eradicated.

3.2.2 Choice of Inert Material.

The importance of the correct choice of inert material in obtaining satisfactory differential thermal results is frequently overlooked. The primary requirement is of course, that the material chosen should give no thermal effect in the temperature range used. Calcined alumina is by far the most commonly-used inert material. Grimshaw (1945) and Mackenzie (1952) have obtained reasonable results by using part of the sample precalcined to 1000°C as the inert material for work on clays. It seems that the most suitable inert material may be dictated by the materials under investigation. However, whatever is used, the particle size should be similar to that of the specimen.

3.2.3 Weighing of Sample.

Most apparatuses require about 0.2-0.5 gram. Mackenzie and Farquharson (1953) found that, other factors being constant, peak temperatures for 0.2-1.0 gram samples could be reproduced quite readily.

The weight of samples used in investigations in this laboratory is in the range 0.2-0.5 gram. Samples are weighed on a small watch-glass, the sample is packed into the cell and the difference in weight after this operation is taken as the sample weight. Great care is needed in this procedure to ensure that all the sample is packed into the cell and not scattered near the edges. Once more it is a matter of practice by the operator to ensure correct weighing.

3.3 Packing of Sample

Lack of uniformity in packing may lead to base-line drift because of differences in the thermal diffusivities of the specimen and the inert material. Arens (1951) has concluded that the effect of variation in packing would be greater at low temperatures since at high temperatures heat transfer would be largely effected by radiation. Packing by means of a glass plunger has given reproducible results in investigations by the author. It is doubtful whether two operators could achieve exactly the same degree of packing, but McConnell and Early (1951) have shown that by careful tamping, reproducibility in packing to within one per cent can be achieved.

3.4 Heating Rate

The heating rate of the sample affects peak width as well as peak temperature. On the curve for temperature difference against time, slow heating rates give broad shallow peaks while fast rates give narrow peaks. Speil (1945) showed that peak areas are not affected. On the more usual curves for temperature difference against temperature however, the peaks vary considerably in area and those obtained with slow heating rates are much smaller and sharper than those with fast heating rates.

The heating rate employed by investigators varies from 0.5°C per minute to 200°C per minute. The heating rate in this laboratory is 400°C per hour. This rate was chosen to enable comparison of results with those obtained on the Stanton Thermobalance which is often used in conjunction with d.t.a. investigation.

In comparing results from different equipment, it is essential to know the heating rates and whether or not they are uniform.

4. APPLICATIONS OF D.T.A

4.1 Quantitative

Sewell and Honeyborne (1957) point out that a theoretical study of the mechanism of differential thermal analysis may be expected to prove useful in practice by :-

(i) Revealing causes of base-line drift and indicating how it may be reduced to a minimum.

(ii) Establishing a relationship between the area of a peak and the heat evolved or absorbed in a reaction, thus providing a basis for quantitative work.

(iii) Showing the extent to which variations in heating rate, size of test sample, type of crucible, etc., affect the position of a reaction peak, thus making possible a rational comparison of the results obtained with different types of apparatus.

All such studies can only be applied to simple reactions such as:

(i) Reversible phase changes exemplified by the $\alpha \rightleftharpoons \beta$ inversion of quartz

(ii) Thermodynamically irreversible decompositions obeying a first-order law: the fairly common type of reaction in which the rate of diffusion of a gaseous reactant or resultant is the controlling factor appears too complex for a general treatment to be useful.

However, following other investigators Sewell (1952) has shown that the peak area is proportional to the heat of reaction per unit mass of active sample, and provided that constant conditions are maintained, heat of formation of compounds may be determined. For any apparatus to be suitable for this purpose, many samples of compounds of known heat of formation must be used and examined to give standard size peaks.

This work is complicated by the occurrence in some cases of overlapping peaks. Speil (1945) has shown theoretically that the total area of the joint peak is equal to the sum of the areas of the peaks which the reactive components would give if diluted to the same degree with such inactive materials as will produce mixtures with the same conductivity.

4.2 Qualitative

The qualitative uses of d.t.a. are many. Le Chatelier (1897) was one of the first investigators to realise the possibilities of the method in determining clays. Each clay and mineral gives characteristic differential curves at specific temperatures when heated. This effect finds particular application in mineralogical studies.

In inorganic chemistry, valuable information may be obtained on the behaviour of compounds when heated. Considerable time may be saved obtaining a differential trace showing the temperature at which a compound decomposes instead of a laborious study by heating at various temperatures and then analysing products and residue. This method also finds application in solid-state chemistry. The determination of the temperature of the reactions of lime with clays has been of great value in the cement industry. Self diffusion studies, examination of precipitated hydroxides and activity of catalysts are some of the applications.

The use in ceramics, and organic chemistry also, shows the versatility of the method.

Controlled atmosphere d.t.a. with various gases also has wide application. However the furnace now in operation would be difficult to convert for this method.

5. ACKNOWLIDGEMENT

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