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APPLICATION OF THERMAL ANALYSIS IN SCREENING FOR CHEMICAL PROCESS HAZARDS

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ABSTRACT

The testing of substances and reaction mixtures for the prevention of process hazards poses special problems, which may be solved, to some extent, by commercial DTA and DSC equipment. The standard equipment specially designed for dynamic, isothermal and constant volume tests and the testing procedure is described. Finally, the principle of an evaluation method is briefly outlined.

INTRODUCTION

Thermal explosions are one of the major hazards in the chemical industry. They occur in condensed systems, not reacting under normal conditions to any appreciable extent. The reaction is started by increasing the temperature.

If the reaction is exothermic and the heat evolution is greater than the heat losses, then the temperature will increase until all reactants are consumed. It is a reaction "autocatalysed" by heat. At higher temperatures, the reaction mechanism may change and another, perhaps more exothermic, reaction may be started. Huge quantities of vapours or gases may be evolved and at some point the reaction velocity may be so high that we call it an explosion.

An explosion of a great mass of material causes great damage to personnel and equipment and can cause lasting pollution of wide surroundings. To prevent such accidents, every reaction which is to be performed on a large scale must be examined along the following lines.

(1) Is the desired reaction exothermic or endothermic? In the research stage of a new synthesis, even this fundamental fact is often not known.

(2) Are any parasite exothermic reactions possible at higher temperatures?

(3) What is the decomposition temperature?

THEORY

Most papers dealing with the evaluation of thermal analysis data express the dependence of the reaction velocity on temperature by means of the Arrhenius equation[1, 2]. As far as it holds, no decomposition temperature can be defined, as the reaction constant has a positive and finite value at any temperature above absolute zero. The temperature at which the slowly proceeding reaction is detected depends mainly on the sensitivity of the instrument.

Draper and his collaborators[3] proposed another theory of heterogenous reactions, according to which the Arrhenius equation is not at all applicable to heterogenous reactions; the reaction starts at that temperature, at which its free energy change passes zero to become negative. In that case, the decomposition temperature is thermodynamically precisely defined, and neither kinetic inhibitions nor induction times should exist.

Most decomposition reactions being irreversible, the decomposition temperature cannot be calculated from thermodynamic data in a simple way, but, according to Draper[3], it may well be measured by thermoanalytical methods. Draper supposes that every reaction starts with an endothermic step, i.e. the breaking of the existing bonds of the reactant. This step is governed by the heat transfer kinetics from the surroundings to the sample. Only the next step, the formation of new bonds, can cause the whole reaction to be exothermic. For endothermic decompositions, his calculations agree pretty well. An experimental separation of the two steps in the case of an exothermic reaction is practically impossible, which again renders the determination of the decomposition temperature uncertain.

As none of the existing theories of reaction kinetics can give us a reliable definition of the decomposition temperature, a practical definition, compatible with the measuring techniques, has to be introduced. The decomposition temperature is defined as the lowest temperature at which a spontaneous temperature increase has been observed in a defined apparatus under defined conditions in the course of a defined period of time. The apparatus will be described in the next paragraph.

EXPERIMENTAL

DTA and DSC methods

The thermal behaviour of substances and reaction mixtures may be studied by any DTA or DSC apparatus. The advantage of these methods is the small sample size needed, typically a few milligrams. With this quantity, even a highly explosive substance may be tested, whereas a quantity of even 1–2 g in a test tube could cause serious damage.

Another advantage lies in the time required for the test. A test is run in 1–2 h or even less, depending on the temperature range in question. These characteristics make the DTA/DSC methods ideal for first examinations of unknown products or reaction mixtures. For a more detailed examination, these characteristics may show themselves as disadvantageous.

A sample of a few milligrams taken from a grossly heterogenous suspension cannot guarantee that its composition is representative for the whole mass. Homogenisation methods used in microanalytical chemistry are not applicable, as by changing the crystal size, the reactivity of the mixture will be changed. The observed

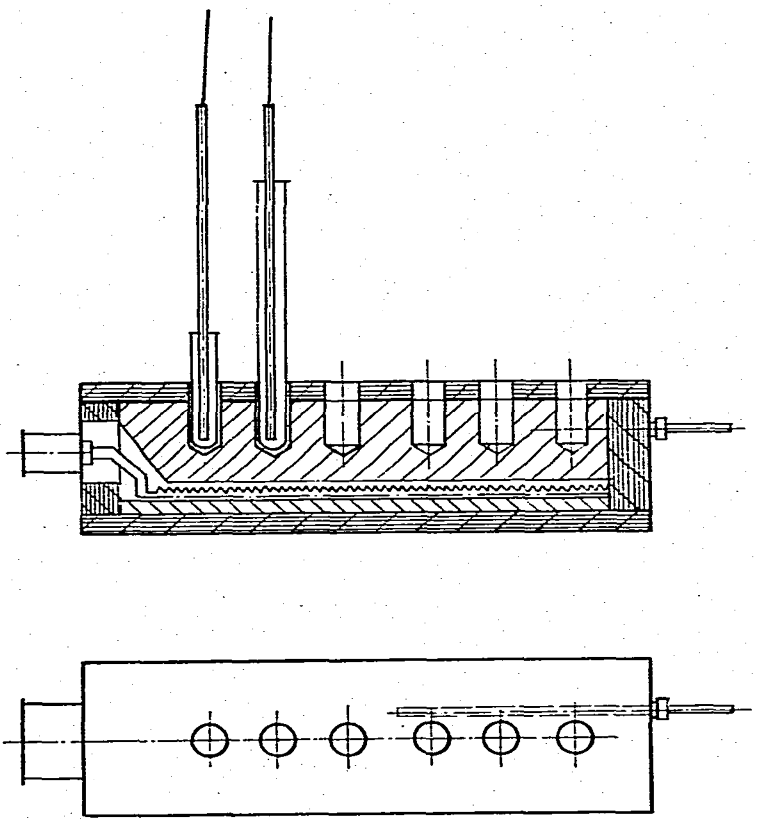

Fig. 1. The Geigy–Kühner apparatus for dynamic decomposition tests.

beginning of an exothermic reaction, i.e. the first deflection from the zero line, is a function of the heating rate, shifting towards lower temperatures at lower heating rates. The shift depends both on the properties of the apparatus used and on the properties of the sample, so that no standard correction can be introduced.

DSC and DTA being essentially dynamic methods, their sensitivity decreases with decreasing heating rate; the slowest heating rate applicable with these apparatuses is still unrealistically high in comparison with the rate at which a production vessel can be heated, so that DTA data on decomposition temperature are not a reliable basis for a safe production process.

The Geigy–Kühner test

A simple test has been developed by Lütolf in the laboratories of the former I. R. Geigy in Basle. The apparatus, constructed in collaboration with A. Kühner, was described as the Geigy–Kühner apparatus[4] (Fig. 1). It consists of a metal block with a heating element and a temperature controlling unit, which enables either a linear heating rate of 2.5°C/min, or a constant temperature to be maintained. In the block there is a row of holes in which standard test tubes containing 2 g samples may be placed. The temperature is measured in the sample by an iron–constantan thermocouple, protected by a thin glass tube. In the original version, the temperature of the sample and that of graphite as inert reference substance were recorded simultaneously. To increase the sensitivity, the temperature difference between the sample and reference (graphite) is now usually measured. Thus, the apparatus is essentially a simple DTA apparatus with rather large samples (2 g).

The test programme comprises first the *dynamic test* with heating rate 2.5°C/min, which furnishes a quick orientation of the properties of the sample. In the following *isothermal test*, the block temperature is held constant 10°C below that, at which an exothermic reaction has been observed in the dynamic test, and a fresh sample is put into the preheated block. Its temperature rises very steeply, and if it exceeds the reference temperature and forms a peak, the experiment is stopped and the block temperature is again lowered by 10°C. Then a fresh sample is put in. This is repeated until no exothermic peak appears during eight hours. The last temperature at which an exothermic reaction is observed is then the "isothermal" decomposition temperature. From this value, a security interval of 50°C is usually deducted to determine the highest temperature for safe handling of the product. If, for some technological reason, the substance or reaction mixture must be exposed to temperatures nearer to the decomposition temperature, a more detailed examination by calorimetry must be performed. A calorimeter suitable for such tests has been described by Perron and Regenass[5].

The isothermal bench

In one block with six holes, described previously, five dynamic tests can be run simultaneously. In the isothermal test, however, the block temperature must be adapted for each substance separately, and the testing capacity is very low due to the long testing time. To increase the testing capacity, to simplify the manipulation, and to reduce the time of examination, a new apparatus has been constructed in the laboratories of Sandoz[6].

A long aluminium block (Fig. 2) is heated at one end to 350°C, while the other end is cooled by tap water. With proper thermal insulation, an almost linear temperature gradient is formed along this block. Two rows of holes are drilled in it at distances corresponding to steps of 10°C. A special sample holder for 10 test tubes with probes

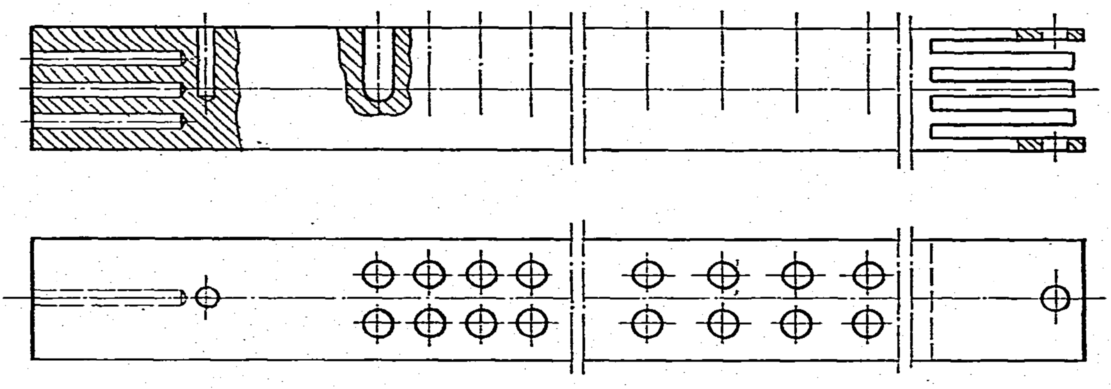

Fig. 2. The Sandoz apparatus for isothermal tests.

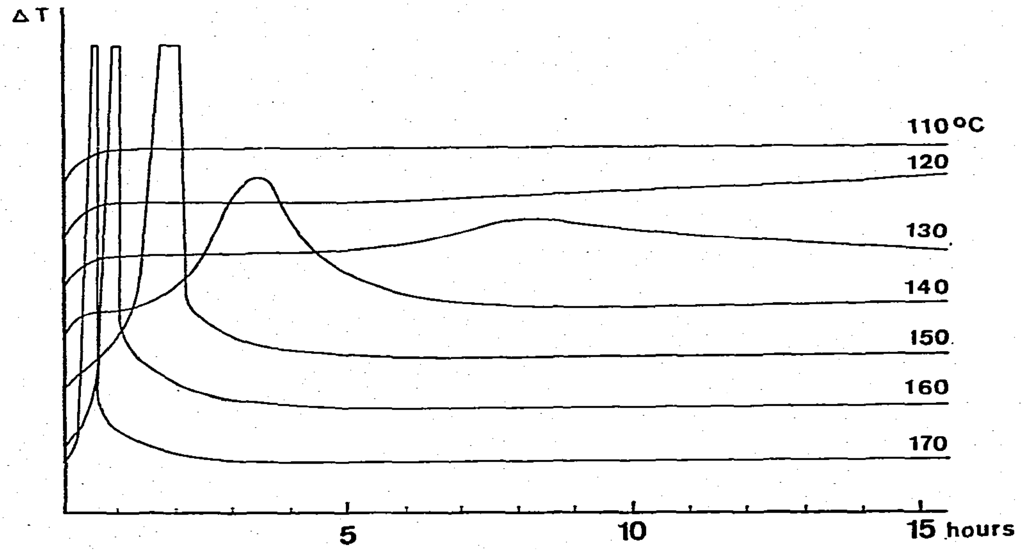

Fig. 3. The isothermal decomposition curves of *p*-chloro-*o*-phenylenediamine at various temperatures. (The curves at 100 °C and below are omitted for the sake of clarity.)

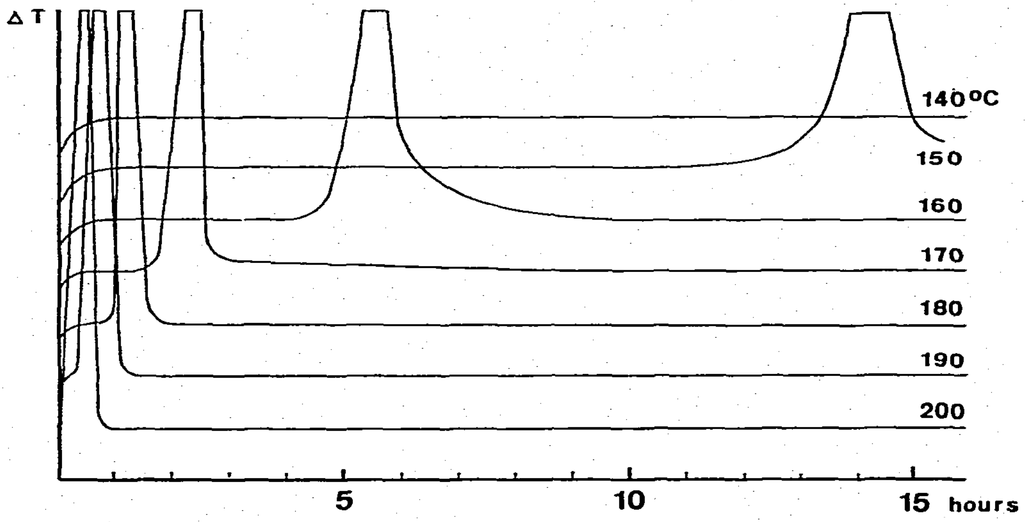

Fig. 4. The isothermal decomposition curves of endrin. (The curves at 130 °C and below have been omitted.)

and 10 tubes with graphite is then put in at the place where the highest temperature is 10 °C below that determined in the dynamic test. The temperature differences of the 10 pairs are then recorded simultaneously on a multichannel recorder. We obtain a record (Fig. 3) which shows the typical sequence of exothermic reactions with decreasing maxima. The decomposition temperature, according to our definition, may be determined in the course of one experiment.

Some substances react with almost the same intensity at lower temperatures, but the induction period increases (Fig. 4). We may speak about induction times here, because a retardation of several hours cannot be explained by slow heat transfer to the

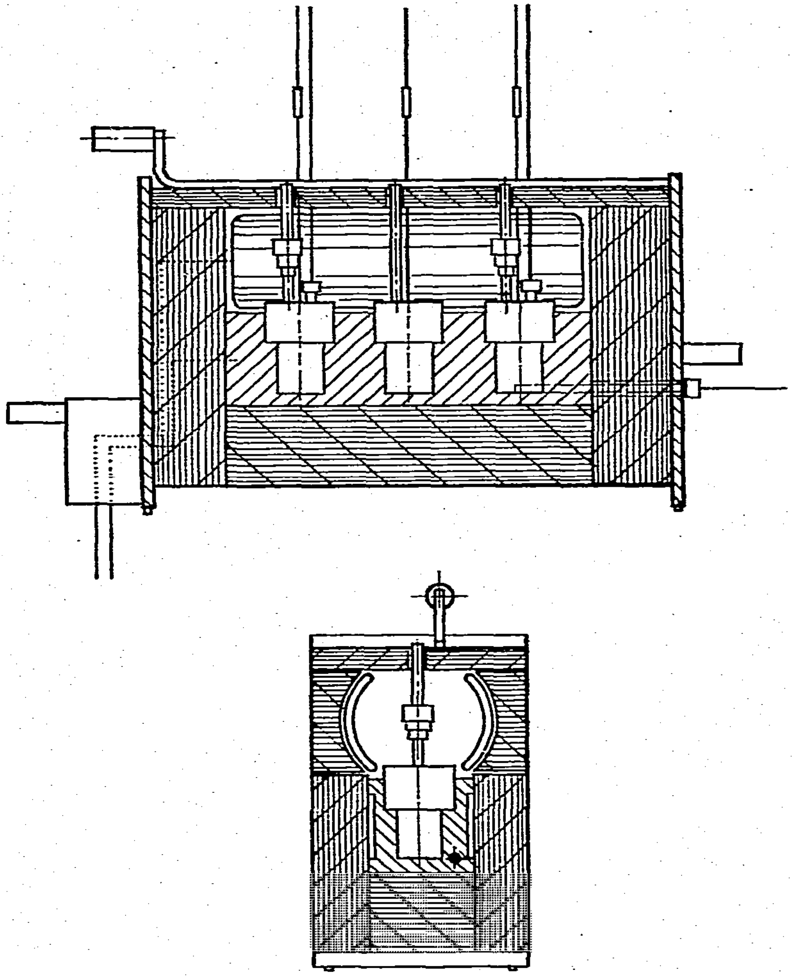

Fig. 5. The miniautoclave for decomposition tests in a closed volume.

sample. In some cases, a linear dependence of the logarithm of the induction time on temperature has been observed.

The miniautoclave

If the sample contains a solvent or some other volatile component, the strongly endothermic reaction of evaporation may overlap an exothermic reaction. As the sample is to be examined at least 50 °C above the desired temperature of treatment, the effect of evaporation must be eliminated. For this reason, the Geigy–Kühner apparatus has been modified[7] (Fig. 5). The block has only three holes of large diameter, and two samples and a reference are placed in identical miniature autoclaves, with provisions for temperature and pressure measurements.

The reference temperature, the temperature difference and the pressure are recorded simultaneously for both vessels. The pressure measuring ranges vary from 20 to 500 bar, so that vapour pressure curves may be measured comfortably with this apparatus.

In the case of a decomposition reaction, a sudden pressure increase is observed, accompanied by an exothermic peak. The pressure measurement may be used to indicate a slow reaction under isothermal conditions.

EVALUATION METHODS

The questions concerning the sign of the reaction heat and the parasite reactions may be answered directly from the DTA or DSC curve or from the dynamic Geigy–Kühner test. The decomposition temperature may be determined directly from the isothermal test record.

In many cases, these data are sufficient for the determination of the safe operating conditions. If the temperature range so determined is disadvantageous for technological reasons (reaction too slow, low conversion grade, unwanted side-products), a calorimetric study must be performed, as mentioned earlier. Another possibility is the evaluation of the test by the method developed by Kobler[8]. This method operates with temperature differences. First of all, the heat transfer coefficient of the substance in the test tube is determined from a cooling curve. The curve of the isothermal test is then numerically integrated and the maximum temperature which would be reached under adiabatic conditions calculated. Then, the adiabatic temperature profile may be expressed as a function of time, with the starting temperature as parameter. The heat evolution rate can thus be calculated for various starting conditions.

These data are then compared with the known cooling capacity curves of the reaction vessel to be used. As a result, the maximum admissible batch volume for which the reaction can be held under control by cooling is determined.

REFERENCES

1 J. Sestak, *Thermochim. Acta*, 3 (1971) 1.
2 D. Krug, *Thermochim. Acta*, 20 (1977) 53.
3 A. L. Draper, *Proc. 3rd Toronto Symp. Therm. Anal.*, 1970, p. 63.
4 J. Lütolf, *Staub Reinhalt. Luft*, 31 (1971) 93.
5 W. Perron and W. Regenass, *Proc. 1st Eur. Symp. Therm. Anal., Salford*, 1976, p. 73.
6 G. Pellmont, Sandoz AG, Basle, unpublished results.
7 M. Pochon and M. Futterer, Zersetzungsprüfung nach Geigy–Kühner in einem druckfesten Behälter. Internal Report, Lonza AG, Visp, Switzerland, 1973.
8 A. Kobler, Die sicherheitstechnische Charakterisierung der Startphase einer Exothermie durch Computerauswertung ihres im offenen und geschlossenen Prüfgefäss digital erfassten Thermogramms. *Internal Report RC 62 509*, Hoffmann-La Roche Ltd., Basle, Switzerland, 1976.