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ADIABATIC METHODS FOR THE INVESTIGATION OF EXOTHERMIC REACTIONS

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SUMMARY

For the investigation of exothermic reactions, especially decomposition or runaway reactions, adiabatic test methods are important and often necessary. The most simple adiabatic method is the Dewar method. The thermal insulation by a Dewar flask can be replaced by an electronically controlled adiabatic shield. The combination of a Dewar flask with a controlled adiabatic shield seems to be the best method. For exothermic reactions which proceed above the normal boiling-point, methods involving closed vessels or a Dewar flask under inert gas pressure are used.

From adiabatic temperature-time curves heat production and reaction rates can be evaluated. For decomposition reactions the reaction rate usually depends on the conversion, and the kinetic evaluation can be difficult. But the determination of induction periods can be very important for safety considerations, and the adiabatic induction period, plotted on a logarithmic scale versus the reciprocal absolute temperature, yields a straight line from which a characteristic decomposition temperature can be deduced.

The usefulness of an adiabatic method depends on heat transition to the environment, e.g. characterized by a halflife time of a Dewar flask, and the heat capacity of the apparatus in which the heat capacity of the vessel is compensated using a computer controlled heating proportional to the self-heating rate. So the true self-heating can be recorded independently of heat capacities of the instrument.

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INTRODUCTION

By adiabatic methods the self-heating of substances or mixtures by exothermic reactions is investigated. Thus the real thermal explosion can be observed which is slow at first and is accelerated by the rising temperature. The rate of temperature rise is to a first approximation proportional to the rate of heat production and to the rate of the exothermic reaction.

In simple cases the total temperature increase by the adiabatic reaction is proportional to the heat of reaction. The rate of reaction can directly be calculated from the rate of temperature rise. But strong exothermic reactions often result in throwing the thermocouple out of the apparatus together with the foaming product. So the maximum temperature of self-heating cannot be measured.

All methods are equivalent which obtain adiabatic conditions by different devices. The existing methods can be classified into the following sections:

1) Dewar methods
2) Methods using controlled adiabatic shield
3) The combination of (1) and (2)

The last method is the best of all.

EXPERIMENTAL METHODS

Dewar methods

The simplest experimental setup is shown in fig. 1. The Dewar flask containing the sample is placed in an oven (e.g. a drying oven). The temperature in the substance and in the oven is measured by thermocouples and a temperature recorder. The temperature distribution in the oven should be as uniform as possible, and the Dewar flask should have good insulating properties.

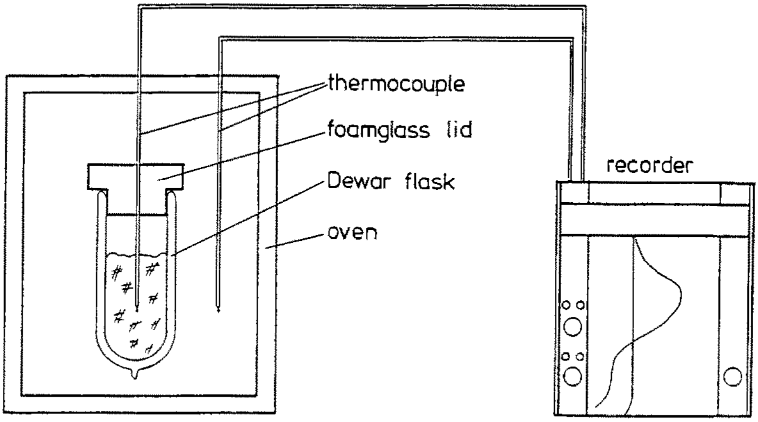

Fig. 1. Simple Dewar flask test setup

The following suggestions may be helpful in conducting the experiments. It is advisable to test the insulating capacity of the Dewar flask by filling it with a heated substance (such as water) and recording the cooling curve with the vessel in a normal-temperature environment. It is important to close the Dewar flask with a highly insulating lid, since a well-insulated Dewar flask loses heat almost exclusively through the opening. Lids made of temperature-resistant foam, such as foamed glass, have been used successfully. Normal Dewar flasks frequently lose their insulating capacity if they are exposed to temperatures in excess of 200 °C. However, it is possible to obtain from the manufacturers specially heat-treated Dewar flasks which will withstand temperatures over 200 °C without any loss of insulating capacity.

We should also point out here the dangers to which the experimenter may be exposed because the exothermic reactions of some substances or mixtures finally become so violent that the Dewar flask and possibly also the oven are destroyed. This should be taken into account in designing the experimental setup. When the test amounts are a few hundred grams or more, the experiment should be conducted with the application of special safety measures (preferably behind a protective wall). This is the reason why we and other experimenters prefer to use the smallest possible amounts.

If the selfheating process being studied begins around or above the boiling point of the sample, it is no longer possible to work with the open Dewar flask as shown in figure 1. For these cases the following experimental arrangements have proved successful:

a) sealed glass ampoule in the Dewar vessel,
b) steel pressure vessel in the Dewar vessel,
c) Dewar vessel in an autoclave under inert gas pressure.

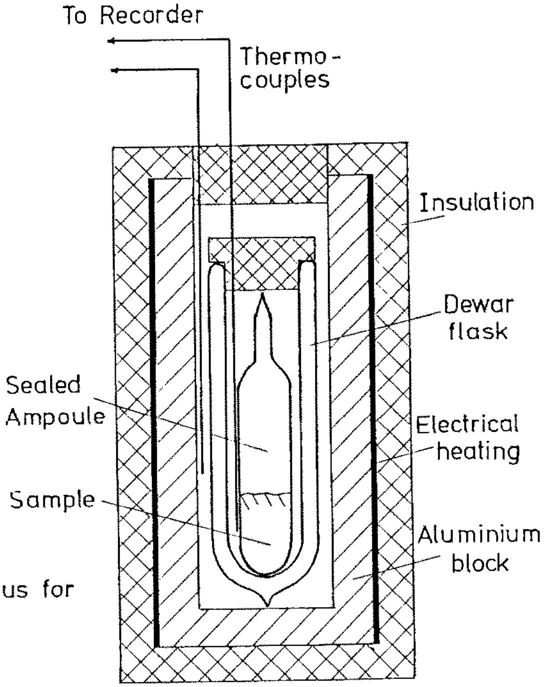

Fig. 2. Dewar flask test apparatus for substances decomposing above normal boiling point

Setup (a) requires only relatively simple apparatus [2, 3]. It is important to have a strong oven with a vented opening, which should be directed upward. In a "successful" trial the glass ampoule usually bursts and the Dewar vessel is destroyed. We have had good success with the arrangement shown in figure 2; its most essential feature is a strong aluminium block with built-in heater and insulation. It is set up where it can vent upward without causing any damage, as in a stable fume cupboard.

An advantage of the method is that it can be used for aggressive and corrosive substances. Its disadvantages are that no pressure measurement is possible and that the ratio of the heat capacity of the sample to the total heat capacity is unfavourable small.

Experimental arrangement (b) was developed by Berthold and Zieger [4]. The apparatus consists of a 1-litre special-steel pressure vessel with a bursting disk which responds at 50 bar. This vessel is placed in a Dewar vessel and both are enclosed in a larger pressure vessel. The pressure curve can be recorded, at least during the first stage of the exothermic reaction. The large pressure vessel serves to fully contain the reaction products and other materials after the bursting disk responds. The ratio of the heat capacity of the sample to the total heat capacity in this method is even more unfavourable than for apparatus (a).

In method (c) an attempt is made to prevent the substance from boiling by increasing the ambient pressure. Since the Dewar flask must withstand this increased pressure, only rather small Dewar flasks can be used. Our experimental arrangement [5], which is depicted in figure 3, employs 200 cm^3 Dewar vessels that will withstand an external pressure of about 10 bar.

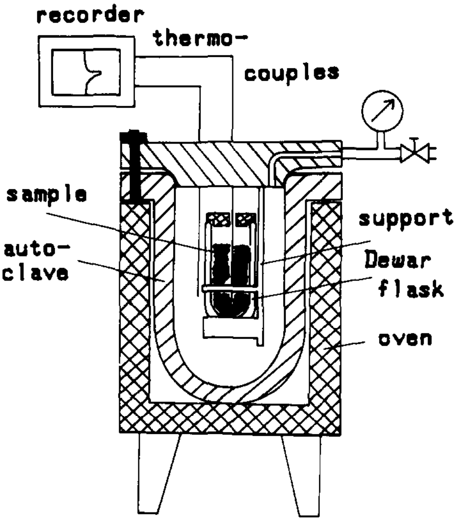

Fig.3. Dewar flask test under inert gas pressure

We also use Dewar vessels which are made of double-strength glass (approx. 3 mm) and which consequently are suitable for pressures up to about 20 bar. The Dewar flask is placed in an autoclave with a capacity of 5 l. The pressure curve is measured during selfheating, but because of the large volume of the autoclave the pressure rise is relatively small, which has the advantage that the Dewar flask is not destroyed so quickly.

Methods using controlled adiabatic shield

Methods which employ a controlled adiabatic shield instead of a Dewar flask have been described by Hub [6] and Townsend [7]. The instruments developed by these authors are commercially available, and a precise description is given in the prospectus and using instruction of these apparatus. Therefore a description is here not necessary.

A large quantity of control mechanism is required to replace the insulating capacity of a Dewar flask, and no large success is gained by this arrangement.

The ARC (accelerating rate calorimeter) of Townsend has the advantage that small samples of a few grams can be investigated, and the pressure can be measured during the reaction. But the ratio of the heat capacities of the apparatus and the substance is rather large, and the true self-heating of the sample cannot be measured and only be calculated using a dubious theory.

Dewar flask with adiabatic shield

The Dewar test can be made to approach the adiabatic conditions more closely by regulating the oven temperature to follow the sample temperature. The test has been described by Groothuizen, Hartgerink and Pasman [8]. A similar apparatus developed in our laboratory is shown in figure 4. The oven is a heavy aluminiun block which produces a homogeneous temperature distribution around the Dewar flask. For the temperature control, resistance thermometers and a commercial temperature controller were used as has been described by Lemke [9]. The apparatus of Lemke has a liquid temperature bath for heating the Dewar flask. It can work very precisely but only in a limited temperature region.

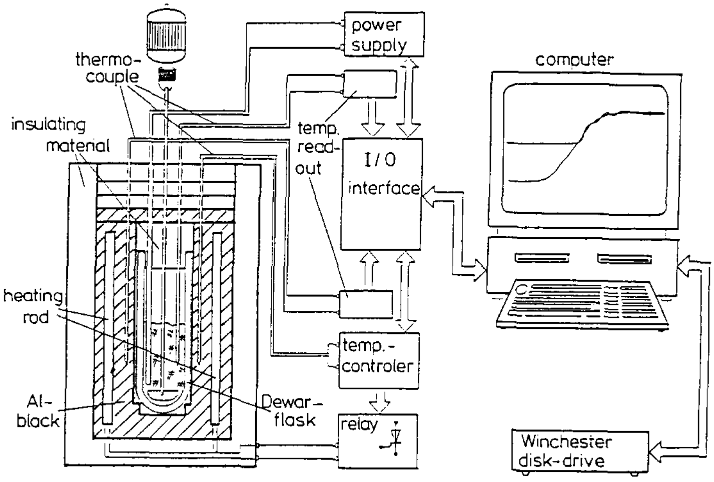

Fig.4. Dewar test with adiabatic temperature control and compensation heating

There are cases in which a following mode of temperature control is essential if realistic results are to be obtained. These are cases in which one exothermic reaction follows another. At the end of the first exothermic reaction the oven temperature must be adjusted to the temperature attained by the substance so that the second stage of selfheating can begin at the elevated temperature level. The same applies, mutatis mutandis, when more than two exothermic reactions follow in succession.

The apparatus represented in Fig. 4 comprises an essential improvement which compensates the mistakes which are caused by the heat flowing to the heat capacity of the apparatus. We achieve this by supplying the heat necessary for heating this "empty capacity", e.g. of the inner wall of the Dewar flask. The "empty capacity" is measured or calculated. As control device a computer is used which provides for supplying the heat proportional to the self-heating rate of the substance.

In this apparatus the temperature rises as fast as in the substance alone without apparatus, and the rather dubious calculation of the ideal self-heating rate of induction period is not necessary. The apparatus in Fig. 4 is supplied with a stirrer for the case that heterogeneous mixtures are to be investigated.

EVALUATION OF ADIABATIC TESTS

The adiabatic tests yield temperature-time curves of selfheating as the primary results. The results are independent of the amount of substance present (if the heat capacity of the apparatus is not important) and are directly applicable to safety in chemical plants. For this purpose the experiments are normally performed.

From the adiabatic temperature-time curve (and the measured or estimated specific heat of the substance) the heat production rate can be estimated which by some people is believed to be important for safety considerations. But for many substances the heat production rate which is proportional to the reaction rate depends on the yield of the reaction as well as on temperature, and the real evaluation of the heat production rate is difficult.

A quantity which can easily be found out from adiabatic temperature-time curves is the adiabatic induction period, the time elapsing between the time the experimental temperature is reached and the time of the most rapid temperature rise (inflection point of the curve). As fig. 5 shows, the adiabatic induction time decreases with increasing temperature. A plot of log τ ad vs. the reciprocal of the absolute temperature 1/T is normally a straight line.

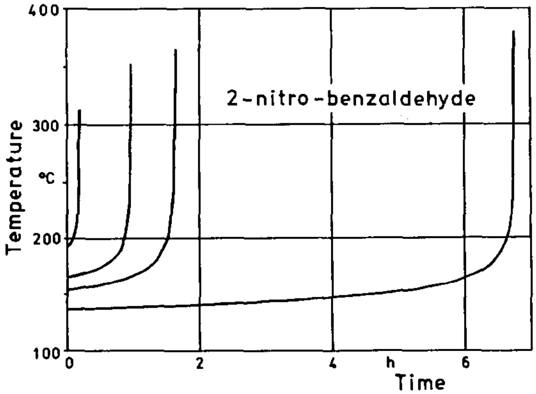

Fig.5. Temperature-time curves of self-heating in Dewar flasks

Each experiment yields a measurement point on this graph. Some people take points at several temperatures in a single experiment, read the time to the inflection point and enter it into the graph, so that an entire curve can be obtained from one experiment. This evaluation is not correct, since for many substances the induction period depends on the pretreatment of the substance, and the induction times taken from the last part of the temperature-time curve are too small. Thus the log τ ad-1/T line becomes too steep. In order to get realistic results it is important to conduct several adiabatic tests starting at different temperatures (storage temperatures) with each substance or mixture.

We have performed Dewar tests on quite a lot of substances. Figure 6 gives results of a special type of compound: substances containing a N-N-bond.

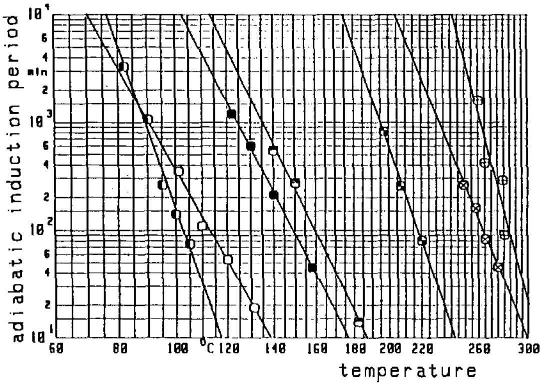

Fig.6. Exothermic decomposition of substances with N-N bonds

Adiabatic induction times versus temperature

⊗ phenylhydrazine
⊖ 1.2-diphenylhydrazine
□ phenyl azide
◐ azoxybenzene
⊕ maleic acid hydrazide
◑ diphenyltriazene
■ azodicarboxylic acid diamide

The adiabatic induction times are plotted in logarithmic scale versus the reciprocal absolute temperature. I would like to take the temperature where the induction time is one day as a safety characteristic date. The "SADT" which has been defined as a transport property for peroxides is not suitable for all substances because it is rather troublesome to be determined.

INVESTIGATION OF REACTION SYSTEMS BY ADIABATIC METHODS

The adiabatic methods are not only useful for the investigation of exothermic effects of substances. Also exothermic reactions which proceed in chemical reactors after mixing several substances can be investigated well by this method. Thus the Dewar method is a competitor of reaction calorimetry.

Hugo [10] has published results of Dewar experiments for measuring reaction rates of exothermic reactions. The evaluation of the results of these tests may be relatively complex. If the reaction follows a simple kinetic law the kinetic constants can be determined.

The runaway behaviour of exothermic reactions can particularly well be studied by Dewar flask tests. A simple setup for tests starting at room temperature is shown in figure 7 [11].

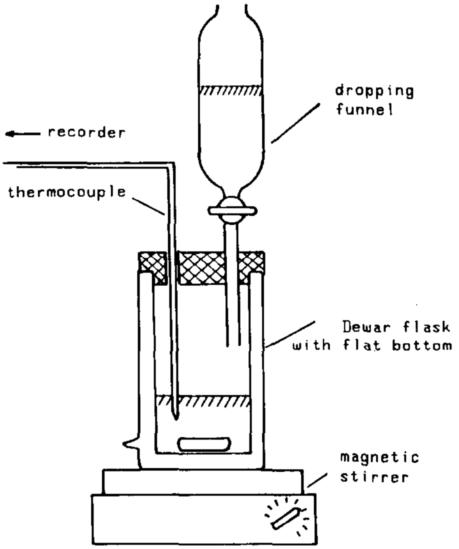

Fig.7. Simple Dewar Test for Reactions

The reaction partners are mixed in a Dewar having a flat bottom. The mixture is stirred by a magnet stirrer. For a higher reaction temperature the Dewar has to be put into an oven. Aluminium block ovens have proved to be advantageous.

The adiabatic temperature-time curve of a runaway reaction is similar to that of exothermic decomposition reactions. In Fig. 8 the self-heating curve of a neutralization reaction is shown.

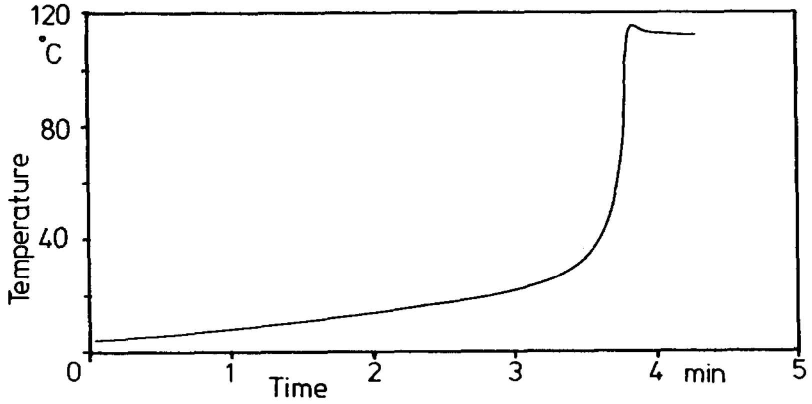

Fig.8. Adiabatic temperature rise by the neutralisation H_2SO_4 (50%) + $2NaOH$ (pellets)

The reaction rate is low in the beginning because the sodium hydroxide - added in form of pellets - dissolves slowly, and the dissolution rate increases with rising temperature. All reactions which are slow at first and become fast with rising temperature can be hazardous in production. An advantage of adiabatic tests is that secondary exothermic reactions which occur in succession can easily be detected and analyzed.

CONDITIONS FOR ADIABATIC OPERATION

The importance of the adiabatic or nearly adiabatic mode of operation, in which results independent of the apparatus are obtained, has already been underscored. It is essential to have a quantitative criterion in order to judge whether an experimental arrangement enables a sufficiently adiabatic mode of operation.

If only short experimental times are required, the simple "oven methods" are also sufficiently adiabatic. The longer the time over which the experiment must run adiabatically, the higher the requirements that must be placed on thermal insulation. The quality of the thermal insulation of a setup can be characterized by a cooling constant or half-life $t_{1/2}$. These variables can be determined by recording a cooling curve with an inert substance such as water.

The cooling of a substance contained in a Dewar vessel, for example, can be described by the following differential equation:

1) $$\frac{d\vartheta}{dt} = -\varkappa\vartheta$$

Where ϑ is the difference between the internal and the external temperatures and $\varkappa$ is the cooling coefficient for the Dewar containing the substance. $\varkappa$ can be calculated from the cooling half-life $t_{1/2}$ means of the equation

2) $\varkappa = \ln 2/t_{1/2}$

If the half-life is determined with water, it must be kept in mind that because of the lower specific heat of the organic substances a smaller half-life must be used in experiments with such a substance.

Table 1 gives typical values of half-lives for different vessels as determined in our laboratory. The half-lives determined with water were converted for a normal organic substance with $c\rho = 1.7$ J/cm³ K. Whereas the half-lives for uninsulated vessels amount to only a few minutes, the considerable value of 8 hours is attained by a 500 cm³ Dewar vessel, for example.

If selfheating follows a purely thermal course (thermal explosion), $t_{1/2}$ represents roughly the length of time within which selfheating occurs approximately adiabatically. If the induction time is longer, a thermal explosion will still occur, but with considerable departure from adiabatic conditions. If the adiabatic induction time is more than four times as long as the half-life, the critical conditions for a thermal explosion will no longer be achieved.

An important factor for evaluating the experimental arrangements is also the ratio of the heat capacity of the sample to the "empty capacity", i.e. the heat capacity of the part of the experimental apparatus which is in direct contact with the sample and takes part in selfheating. In the simple Dewar flask experiment the empty capacity is the heat capacity of the inner wall of the Dewar vessel. Table 2 gives the ratio of the heat capacity of the sample (mass· specific heat) to the total heat capacity (empty capacity + heat capacity of the sample) for a few experimental arrangements. Here the simple Dewar vessels perform relatively the best. In the experimental arrangement in which the sample is enclosed in a pressure vessel which is enclosed in a Dewar vessel this ratio is much less favourable. When the experiments are evaluated this ratio must be taken into consideration if it substantially deviates from 1. In the simple Dewar vessel tests where the heat capacity of the sample amounts to 80 to 90 %, this correction can be ignored as a first approximation.

Table 1

Typical heat transfer properties of sample containers

Container	Volume (cm^3)	$t_{1/2}$ (min) for organic liquid
Test tube	10	3
Glass beaker	100	8
Double-walled glass vessel	200	24
Dewar flask	200	240
" "	500	470

Table 2

Ratio of sample heat capacity mc to total heat capacity W_L + mc

Experimental setup	Dewar flask Volume [cm^3]	$\frac{mc}{W_L + mc}$
Dewar flask	200	0,78
" "	500	0,83
Thick-walled DF	200	0,64
Glass ampoule in DF	500	0,31
Stainless steal vessel in DF	2000	0,26

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