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Equipments for modern thermal investigations

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Abstract

First a report is given about the development of a calorimeter with long-time stability and satisfactory resolution (0.5 mK) for operation in biochemistry under seal or inert gas. It was tested by thermokinetic investigations of the enzymatic hydrolysis of starch. Secondly a DTA for liquid phases with power compensation ("DSC") and with a resolution of ΔT residue of 1 mK is presented. It was successfully applied in the kinetic following up of a reaction between benzene sulfochloride and aniline derivates.

INTRODUCTION

In recent years a series of devices we have developed, which are suitable for experiments under different temperature conditions. These experiments included calorimetric measurements on the one side and DTA or DSC on the other, i.e. the ambient temperature can be hold constant or increased or decreased with time according to a chosen programme.

In all cases our objective was a kinetic evaluation of the measurements in addition to the determination of thermodynamic parameters. Therefore special presuppositions have been fullfilled regarding the choice and the arrangement of the sensors. A further requirement was that the mathematical equations of homogeneous kinetics could be applied. Therefore the reaction chambers were constructed in such a way that a permanent homogenisation of temperature and concentrations could be kept up. Because this is possible only in a liquid medium mixing equipments have been installed in the chambers of measurement and reference. The cell volumina varied between 8 and 60 ml.

The devices of calorimetry and differential thermal analysis described

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below markedly extended our measurement facilities. Together with the development of the nonlinear estimation of kinetic parameters [1] a satisfactory solution arose of the evaluation of thermoanalytical curves.

Wherever possible, we developed digitalized instruments, especially for the following purposes: measurement of temperature, exact automatic control of temperature, programming of heating rate q, measurement of temperature difference, automatic control of compensation power P, storage of measured data. In the following, we are going to describe two of these equipments in more detail.

1. CALORIMETER FOR BIOCHEMICAL LONG TIME REACTIONS

While the thermokinetic follow up of biochemical reactions it can often be observed, that the processes proceed very slowly [2,3], and that, in dependence on the concentration, the change of reaction enthalpy (1-50 J in approx. 50 ml) is distributed over several hours. Often the power of reaction is distinctly below 1 milliwatt per millilitre reaction volume.

Thus we obtain signals in the range of 1 to 100 mK. In order to perform such measurements with the necessary certainty we have developed and tested some aggregates.

- a 40 l thermostat for the range of 285 to 350 K with an accuracy of automatic control of +/- 0.5 mK
- a calorimeter chamber with a volume of 40 - 60 ml
- a milli-Kelvin-meter with a resolution of 0.1 mK

Figure 1 demonstrates the total arrangement. In its centre there is a well isolated water bath of the thermostat (12 cm Piatherm), which is temperature controlled by basic power and additionally by the variable power of the automatic controller. If the desired temperature is below 310 K, controlled cooling by a Peltier battery should be used. The milli-Kelvin-controller (Fig 2) consists of a thermostated brigde circuit (+/- 0.02 K) with a 1000 Ohm silicon sensor (SAS 1000) or 2000 Ohm Pt-sensor in the branch. The deviation from the state of compensation should be given to a chopper stabilized amplifier and further with 10 V/K to a power switch. Thus we used besides of the basic power of 0 to 1000 W, a power driving stage with steering by packets of complete waves by means of variation of the pulse periods. Thus the heater H2 delivers 0 to 30 W and operates in the bath without isolation at 16 volt ac. By switching on/off complete current waves as single or many-fold events steering is effected i.e. automatic power control is done by varying the effective periods of the ac current in the range of 1:10^4 to 1:1 (full power). A LED-display indicates the deviation of control input in units of 0.1 mK. When working below 310 K, a liquid medium cooler on the basis of an 8 W Peltier battery should be employed, whose ΔT command reference is led automatically by the milli-Kelvin-controller.

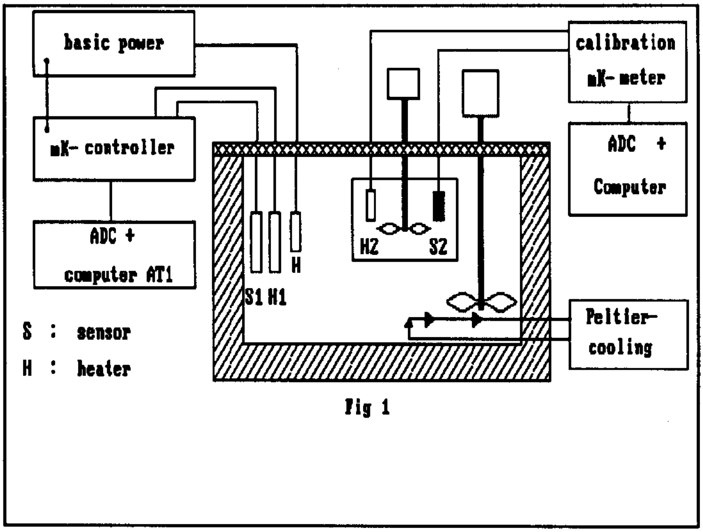

Fig 1

The calorimeter chamber consist of a Dewar vessel which is closed by a stainless steel lid with a PTFE isolation inside.From above were introduced the stirrer, the calibration heater, a guiding heater to make shorter the accomodation period of temperature, the temperature sensor and two filling capillaries for the second reaction component or protective gas. The second component is adapted separately in the thermostat and injected slowly or fast. The velocity of the stirrer is controlled by means of an impulse counter (300 - 600 r.p.m.).

The temperature course in the reaction chamber will be measured by the milli-Kelvin-meter (fig3). The electric circuit is similar to that of the controller but the fine adjustment of the bridge was attained by the helipot 1000 Ohm. To avoid power overloading of the sensor, the bridge was supplied with a pulsed voltage dc in a relation of 1 to 4 at which the mean power over M2 was not larger than 10^{-6} W.

Since the junction at the switches of the resistor decades could generate a parasitic thermo-emf, a pulsed formation of differences was applied in addition, which steadily formed the difference between voltage in measuring and zero state. By this provision the temperature influences at the switches were largely compensated.

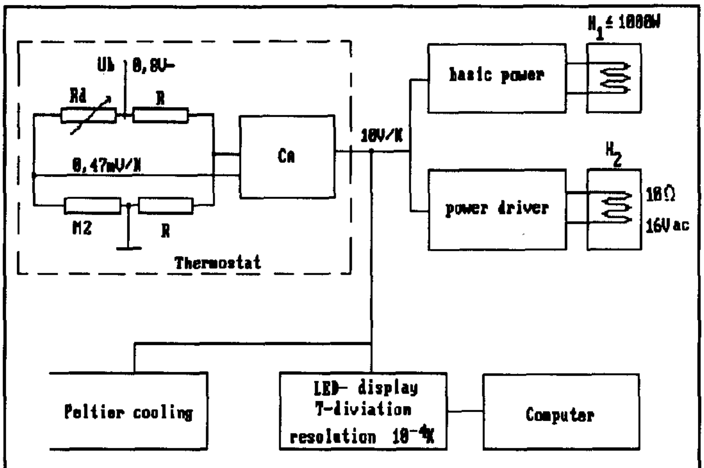

Fig 2

Additionally, the bridge consisting of metal film resistors, the voltage generator of the bridge, the chopper stabilized amplifier and the difference amplifier were thermostated in the range of +/- 0.02 K. The ΔT-display maitained a stability of 10^{-4} K while the12-hours drift of the milli-Kelvin-meter amounted to 1 mK.

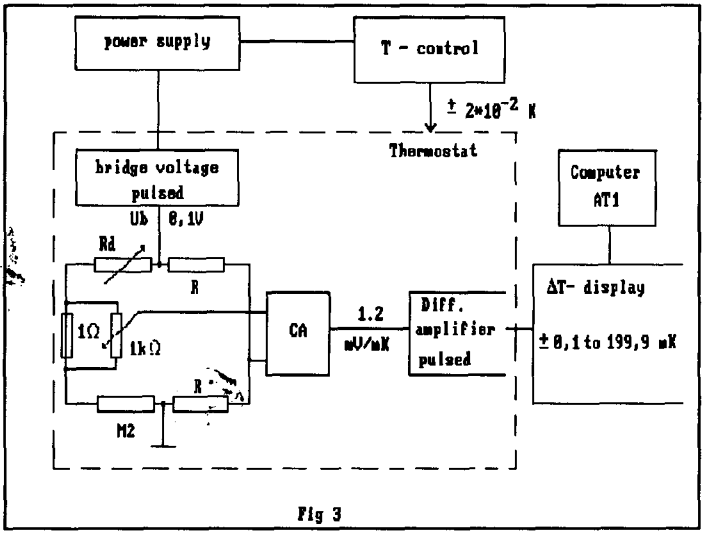

Fig 3

The described calorimeter is well suited for the measurement of reaction heats in organic and biochemistry. It is designed in such a way that undesired atmospheric influences can be excluded using inert gases. Because of the large time of response of the reaction chamber of about 100 minutes a relatively direct follow up of the processes is possible i.e. the heat flux correction after TIAN is rather small in comparison to the heat storage.

In figure 4a-c examples are given for applications of this equipment in biochemistry [4]. Among the enzymatic hydrolysis reactions of different saccharides we have investigated the reaction of potato starch in presence of glucoamylase. Fig 4a shows the calorimeter curve if 1.5 g starch has been treated in 60 ml citrate-phosphate buffer at 58°C by 1 ml GA. As can be seen from the turnover curve 4b, the conversion to glucose is essentially finished after one hour. Accordingly this curve represents the amount of the formed glucose or of the disconnected bonds. An integrated heat production of -43.63 J corresponds to a heat of reaction of about -5.74 kJ per mole formed glucose. This is approximately the same amount we measured for the splitting of one mole maltose.

In Fig 4c the values of the reaction rate calculated on the basis of Borchardt-Daniels equation are shown. Because of the roughness of primary data we had to smooth the curve before we could compute the derivatives. The reaction rate is distinctly higher than that of maltose and decreased in the first 20 minutes to 10 percent of the starting rate.

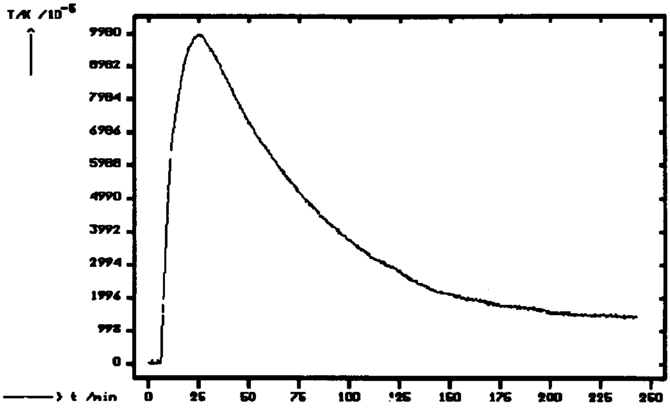

Fig 4a $\Delta T * 10^5$ /K against time /min

2. DTA DEVICE WITH POWER COMPENSATION ("DSC") IN HOMOGENEOUS PHASES

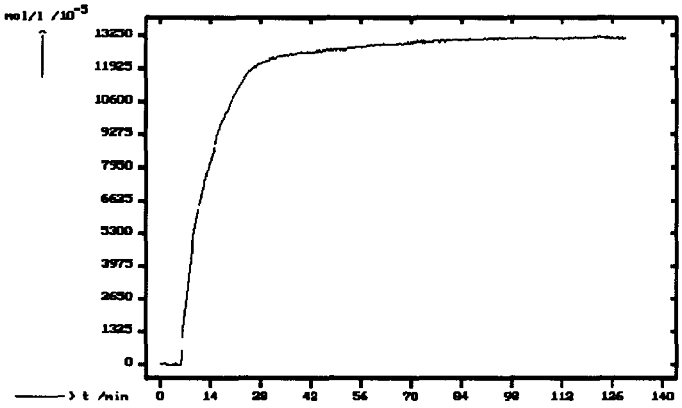

Fig 4b concentration against time

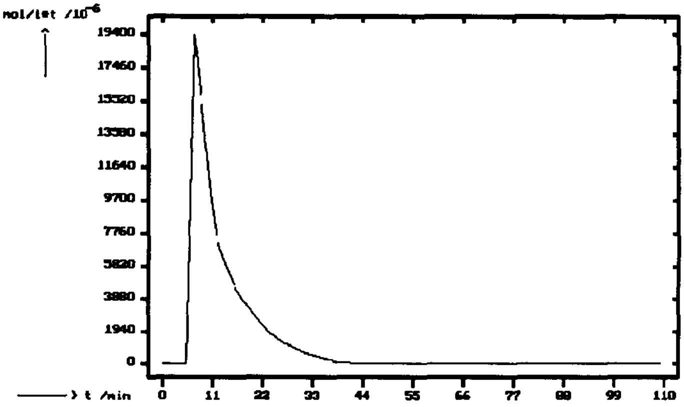

Fig 4c reaction rate aginst time

We have developed an equipment which is suitable for calorimetry (quasi-isothermal) as well as for the DTA in both cases with compensation of ΔT with regard to a reference cell. The measuring and reference cell (MC, RC) are coated inside with PTFE and have a volume of 12 ml. They are suitable for operation under hermetical seal as well as under inert gases. In them we installed small platin stirrers, thermocouples, heater for calibration and compensation and a filling capillary tube. Both cells are enclosed in a metal block. Automatic temperature control (PID-type) was performed digitally at intervalls of one second and was designed for working range between 170 and 420 K. The absolute temperature of the reference cell was recorded by the same computer but phase shifted.

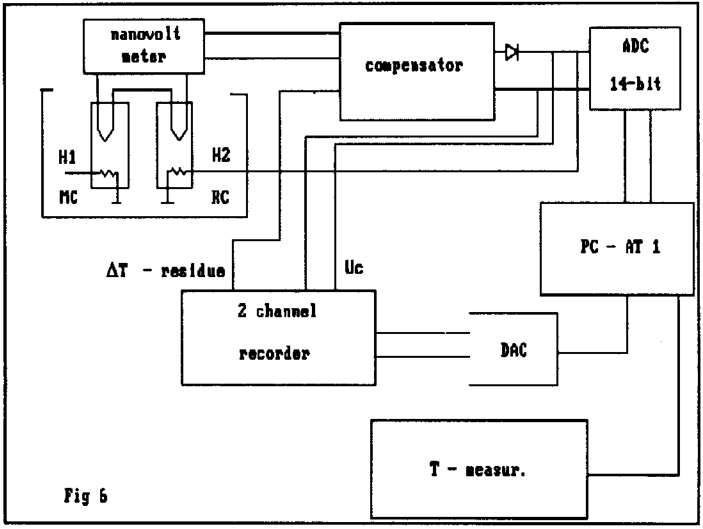

Fig 6

Figure 5 shows schematically the arrangement of the ΔT power compensation whose aim is to lead the temperature difference between both chambers to zero. Therefore ΔT is being measured by a galvanometer amplifier and the signal is passed to the automatic compensator which consists of a difference amplifier with parallel tube mode and a low-pass. The PID-type controller of the compensating power uses a P-stage of 30 dB, an integrative stage of 755 s and a derivative stage of 3.8 s. The summation and power amplifier have an output of 0 to 1 W.

The quality of compensation was recorded by means of remaining ΔT, which could be held at 1 mK. The analogous values of compensation current Ic and voltage Uc were fed into the computer via an analog-digital-converter ADC as well as temperature and ΔT residue. This computer is also responsible for power calculation, monitoring, kinetic evaluation and the parameter filing. For each experiments 6000 pairs of values of power P and temperature T were stored. The threshold of sensitivity is about 1 mW per ml and corresponds to commercial DSC devices. Additionally Uc and ΔT residue were deposit by a 2-channel recorder.

Using special computer programmes it is possible i.a. to find out the reaction enthalpy by integration and the maximum value of compensation power Pmax and its temperature position by differentiation. Here we do not want to enter into details of the kinetic evaluation programmes. Suffice it to say that they require data processing with inclusion of the differential equations. Besides the linearizing methods the better way of nonlinear optimization with simultaneous parameter estimation [1] can be used.

An application of this power compensation technique is given in fig 6, in which the reaction between benzene sulfochloride (0.375 m) with m-chloraniline in a mixed solvent (acetone:dimethylformamide 1:4) is followed up while the temperature changes at a heating rate of 2.3 K/min.

The maximum of compensation is at 0°C and represents a power of more than 0.3 W. By integration the heat production was found to be -456.3 J. According to the increasing rate constant of reaction with increasing temperature a calculation of activation parameters E_A, k_0 and reaction order is possible. We found a second order reaction with 48.1 kJ*mol^{-1} and log $k_o = 9.50$.

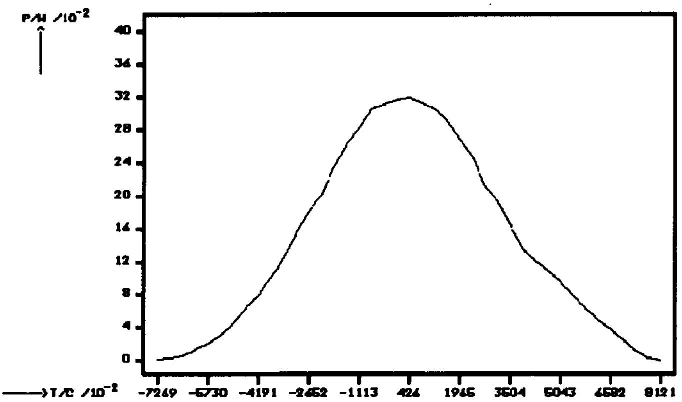

Fig 6 power*10^2 W against temperature *10^2/°C

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