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AN ADIABATIC REACTION CALORIMETER FOR THE DETERMINATION OF KINETIC CONSTANTS OF LIQUID REACTIONS AT HIGH CONCENTRATIONS

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ABSTRACT

The present paper deals with the construction of a highly adiabatic reaction calorimeter for the determination of the kinetic constants of liquid reactions at high concentrations.

The performance of the calorimeter is proved by several moderate exothermal reactions.

1. INTRODUCTION

The calculation of kinetic constants from high-concentration exothermal liquid reaction measurements performed in the adiabatic mode shows substantial advantages over those in the diathermic mode[1–3].

The discussion becomes acute on the question how to compensate the ever present non-adiabaticity, namely shall numerical methods be used to account for or will the experimental set up be taken into account. The numerical approach is extensively discussed previously[3–5].

One of the striking points is the simplicity of the calculations when nearly adiabatic conditions are met, while considerable computer facilities are required in the numerical approach in diathermic experiments.

The condition for the experimental set-up is that only the heat generated by the chemical reaction will be preserved. This means that all temperature effects due to mechanical stirring and convective heat transfer with the surroundings should be balanced.

The rate of temperature change of a chemical liquid reaction in a batch system can be described by:

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$$\frac{dT}{dt} = \frac{Q}{c_p} r(m, T) + \frac{W_s}{C} - \frac{hA}{C}(T - T_c) \tag{1}$$

where $r(m, T)$ is the reaction rate, W_s is the heat of stirring, h is the average heat transfer coefficient, A is the specific heat-exchanging surface area, c_p and C are the specific heat and heat capacity of the system, respectively, and T_c is the ambient temperature.

Since the relative importance of the two smaller terms in eqn (1) varies in the course of the reaction, it is clear that the combined effect of these terms on the calculated kinetic constants will depend on the total length of the reaction time[2]. This effect will be undone by constructing a reaction calorimeter in which the rate of heat production by stirring is compensated continuously by the rate of heat removal due to the heat transfer to a cooling medium of variable temperature:

$$\frac{W_s}{C} - \frac{hA}{C}(T - T_c) = 0 \tag{2}$$

or

$$T(t) - T_c(t) = \frac{W_s}{hA} = \text{constant} \tag{3}$$

Eqn (3) shows that the temperature difference between the reaction temperature and that of the cooling medium is constant and depends only on the heat of stirring and the heat transfer parameters.

There are several methods in realising a cooling medium which gives a constant temperature difference with the reaction temperature. Most frequently, systems are used with electric resistance heating[6-8] but many other principles are applied. In systems with large heat generation the demands on stability and accuracy became insuperable for ohmic dissipation heaters.

The homogeneous heat dissipation of chemical reactions can be used to realise the same temperature rise in the reaction chamber and its surrounding jacket[9, 10]. Richards[9, 10] used an acid-base reaction in the realisation of the adiabatic shield. It is easier and more convenient from the design standpoint to use the same reaction of the adiabatic shield as for the reaction under investigation as will be described below.

2. EXPERIMENTAL

2.1. *The construction*

For the investigation of the thermal stability of continuously stirred reaction systems, the kinetic constants of convenient exothermal liquid phase model reactions at high concentrations must be calculated. This means that the reactor should be able to analyse reactions in concentration ranges of 1 to 3 mol kg^{-1}. Depending on the heat of reaction, temperature jumps of 10 to 40 K can be expected in 10 to 60 min (depending on the reaction rate constants). This results in a rate of temperature change of at most 0.2 K s^{-1}. The operating range is from 274 to 340 K.

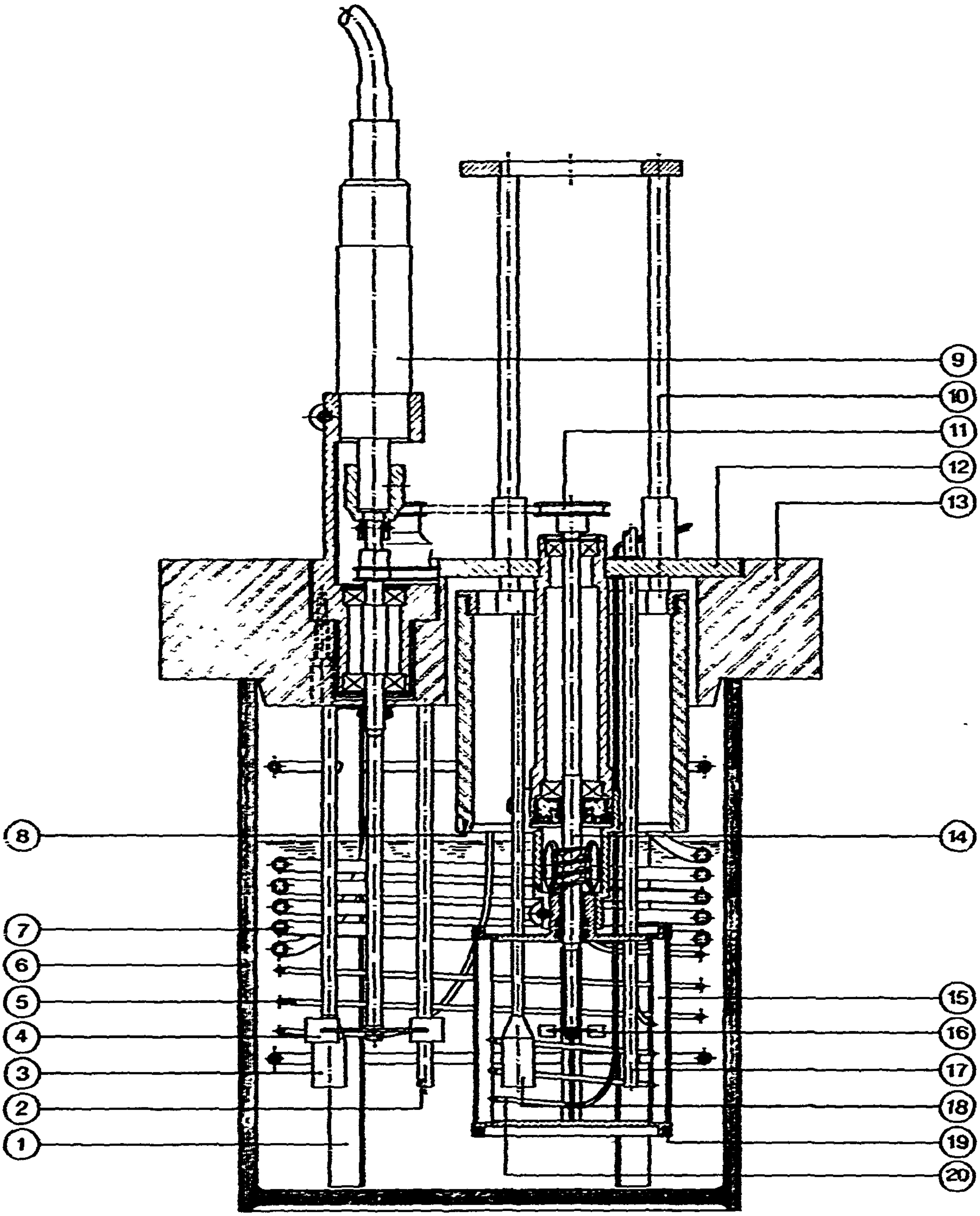


Fig. 1. Sectional drawing of the calorimeter assembly. 1 = Baffles of outer reactor cell; 2 = outer copper temperature sensor; 3 = outer quartz temperature sensor; 4 = turbine-stirrer in outer cell; 5 = thermocoax heating coil in outer cell; 6 = perspex wall of the calorimeter vessel; 7 = cooling coil; 8 = perspex wall of the inner cell; 9 = bowden cable; 10 = support to move the inner cell wall; 11 = spur gear to drive inner stirrer; 12 = bearing top plate of the inner cell; 13 = bearing block of the complete calorimeter; 14 = mixing chamber on the top of the inner cell; 15 = baffles of inner cell; 16 = inner turbine stirrer; 17 = inner copper temperature sensor; 18 = inner quartz temperature sensor; 19 = O-ring to close inner cell when wall is set; 20 = inner heating coil for calibration of calorimeter.

The reactions under consideration for the perturbation experiments are the acid-catalyzed hydrolysis of oxirane and its derivatives, with an expected heat of reaction of 90 kJ mol^{-1}.

For these reasons and those mentioned before the adiabatic shield is realised by using the same reaction as in the measuring cell. If there is no heat exchange with the surroundings and the heat production of the stirrers in the measuring cell and the adiabatic shield balances, the temperature in both will be continuously the same when the experiments are started at the same temperature and with the same concentration. This means, if there is an unbalance in stirring heat production in the measuring cell and the adiabatic shield, there should be a heat leakage through the shield and a possibility of extra heat input into the shield by means of electrical resistance heating.

Figure 1 gives a detailed picture of the reaction calorimeter assembly. The separate parts are accounted for in the figure legend. Only the major design points will be discussed in detail. The inner cell (15) is designed in such a way that it is completely surrounded by the adiabatic shield. To avoid a substantial heat leakage

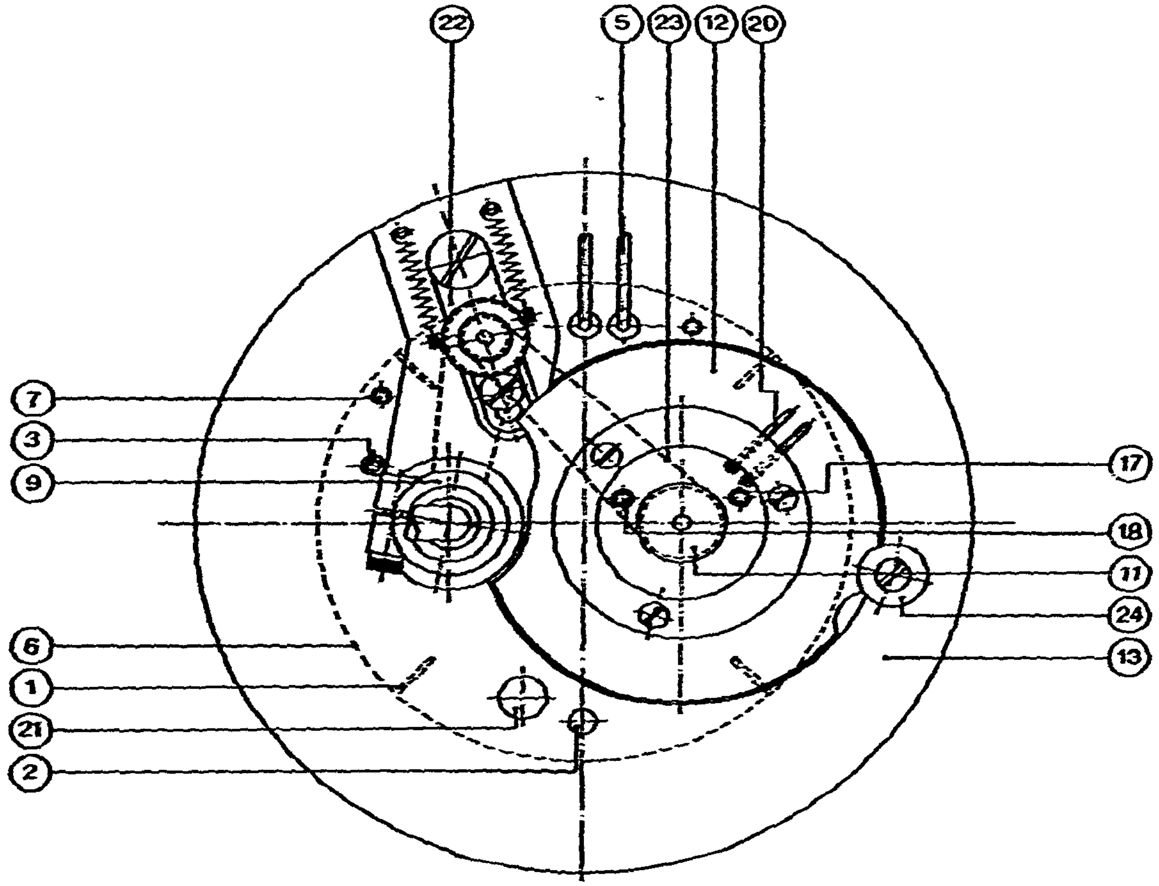


Fig. 2. Top view of the calorimeter assembly. 21 = Position of a combined pH-sensor; 22 = stretcher for the stirring device; 23 = PIC-"no slip" belt; 24 = lock for the bearing plate 12.

through the fastening of the inner cell we constructed a mixing chamber (14) on top of the cell with a screw stirrer in it.

The wall of the cell (8) can be lifted to above the liquid level, establishing a complete mixing.

When the cell is closed, the dynamic behaviour[11] is that of a standard turbine stirred reactor (16). The quartz temperature sensor (18) gives the reaction temperature while the copper sensor (17) indicates the difference with the shield in cooperation with the copper sensor (12) in the outer cell.

All parts of the reactor not made from perspex are silver plated.

In Fig. 2 the drive (9) of the stirrers is shown with its intermediate gear (22) for speed reduction. The stirrer in the outer cell (4) has a speed of 1500 rpm, while the one in the inner cell has a speed of 500 rpm. The intermediate gear (22) serves for the reduction factor and as spanwheel as well.

After releasing the "no-slip" belt (23) and turning the bearing plate (12) the inner cell is unlocked and can be removed from the calorimeter.

2.2. *The data collection system*

To determine kinetic constants as accurately as possible, the number of data points taken during the reaction is in the order of 100 to 200. This means that an

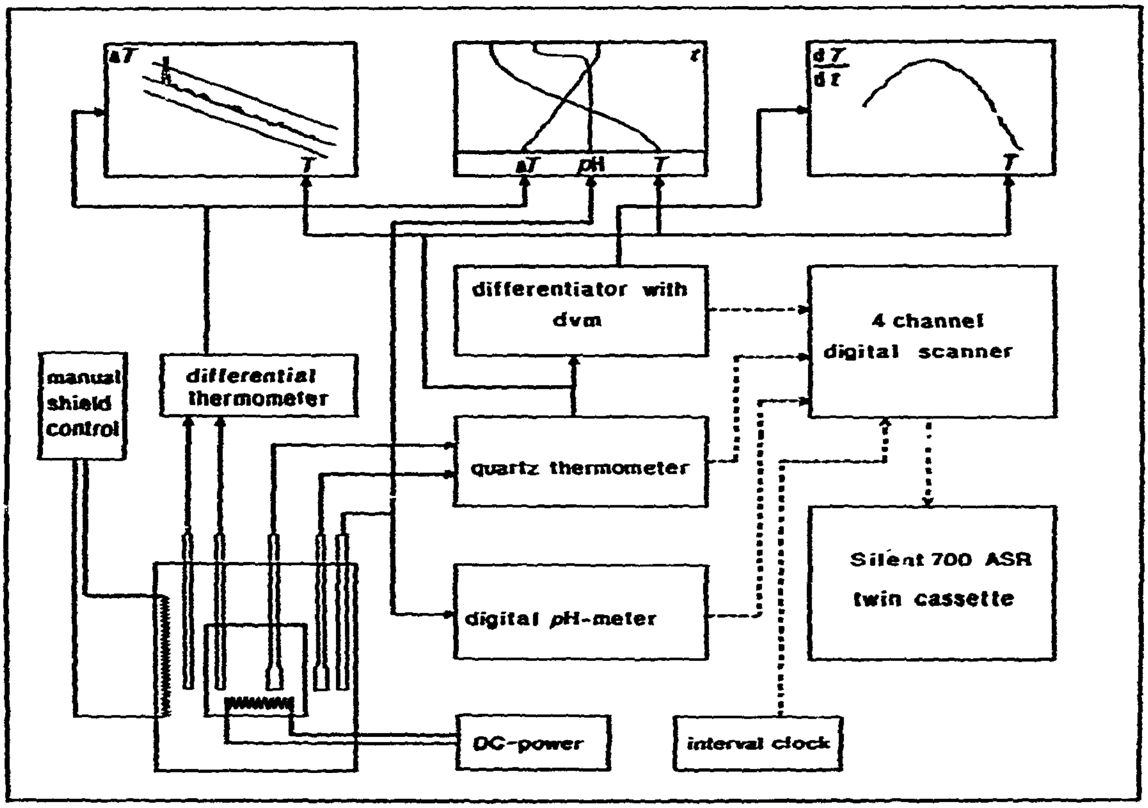


Fig. 3. The data collection and calorimeter control system.

adequate data collection system is necessary. Figure 3 gives a detailed description. Because the Hewlett-Packard quartz thermometer has a digital output just as the pH-meter (Philips PW 9408) we have chosen for a digital scanner (Philips PM 2645). The four digital input channels are scanned successively after a pulse from the interval clock. The data gathered are printed out on paper and written on a digital cassette with a Silent 700 ASR. The first, second and third channel are connected with the pH-meter, the digital output from the temperature differentiator and the quartz thermometer, respectively. The fourth channel is used for a single print-out of the time interval at the beginning of the reaction.

A small adaptation of the quartz thermometer realises a frequency output for the temperature signal. This frequency is converted to a DC-signal and fed to the differentiator and various analog recorders.

The difference between the inner and outer cell is recorded by two copper sensors connected with a Knauer thermometer and fed to the control X–Y recorder. This signal is used to control the power input in the outer cell to establish adiabatic conditions in the inner cell. Although the copper sensors are matched in response and output signal as much as possible, there will be a difference in signal as a function of temperature. Figure 4 gives a typical example of a fairly controlled adiabatic reaction experiment. The straight lines are respectively the stirring heat balancing temperature difference between inner and outer cell as a function of temperature, the +0.01 K deviation line and the −0.01 K deviation line. The curved line is a typical example of the temperature difference signal (ΔT) of a reaction experiment.

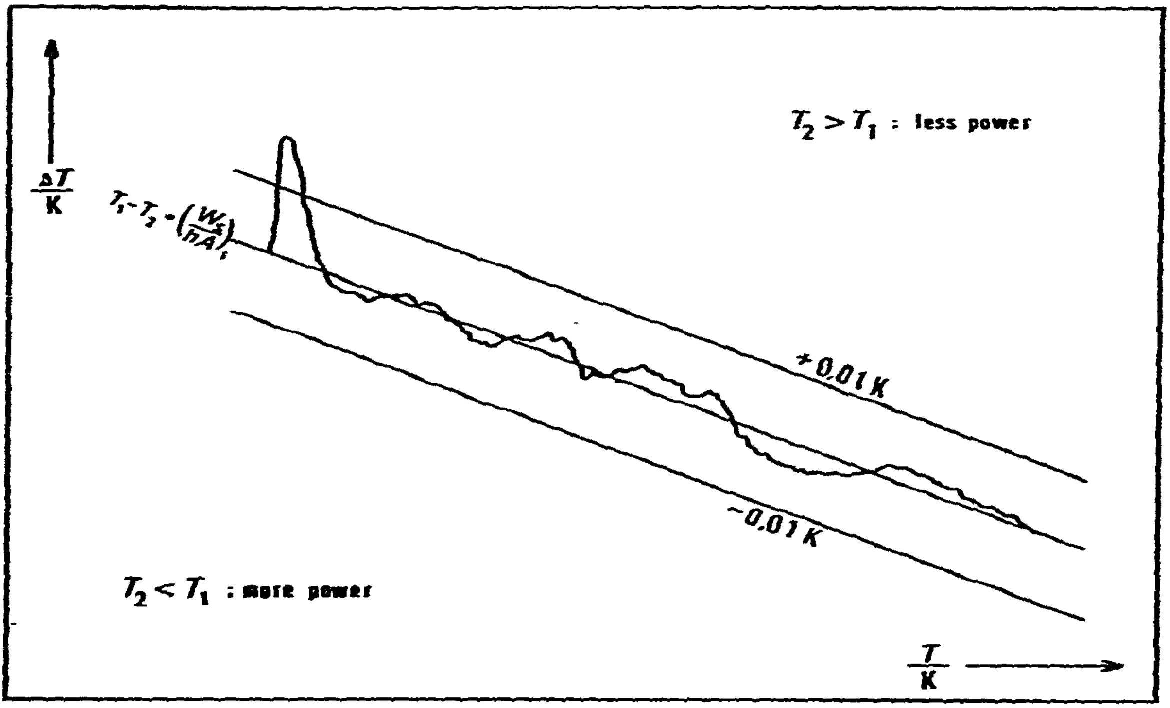


Fig. 4. The control curve for an adiabatic reaction experiment.

Besides the digital registration of the reacting variables there are three analog recorders. A three-pen recorder for the registration of temperature, pH and difference between inner and outer cell as function of time. An X–Y recorder is used for the function of dT/dt versus temperature. The third recorder is the one depicted in Fig. 4.

2.3. *The physical properties*

The dynamic behaviour of the calorimeter is described by the following two equations:

$$\frac{dT_1}{dt} = r(m_1, T_1)\frac{Q}{c_{p,1}} + \frac{W_{s,1}}{C_1} - \frac{(hA)_1}{C_1}(T_1 - T_2) \tag{4}$$

$$\frac{dT_2}{dt} = r(m_2, T_2)\frac{Q}{c_{p,2}} + \frac{W_{s,2}}{C_2} - \frac{(hA)_2}{C_2}(T_2 - T_c) + \frac{C_1}{C_2}\cdot\frac{(hA)_1}{C_1}\cdot(T_1 - T_2) + W_q \tag{5}$$

where the subscripts 1 and 2 stand for the inner and outer cell, respectively. W_q is the nett term to realise the adiabatic conditions in the inner cell, its value can be positive (heating) or negative (cooling).

Under steady-state conditions the differences between inner and outer cell and thermostatted bath are respectively:

$$(T_1 - T_2)_{st} = \frac{W_{s,1}/C_1}{(hA)_1/C_1} \tag{6}$$

and

$$(T_2 - T_c)_{st} = \frac{W_{s,2}/C_2 + (C_1/C_2)\cdot W_{s,1}/C_1}{(hA)_2/C_2} \tag{7}$$

Calibration experiments with $r(m_1, T_1) = r(m_2, T_2) = 0$ but different electrical energy inputs give the possibility of calculating all these constants by normal regression procedures of (dT/dt) versus $(T_1 - T_2)$ and $(T_2 - T_c)$, respectively[2].

These calculations result in:

$$\frac{W_{s,1}}{C_1} = 3.60\cdot 10^{-4}\ \mathrm{K\,s^{-1}} \qquad \frac{W_{s,2}}{C_2} = 7.11\cdot 10^{-4}\ \mathrm{K\,s^{-1}}$$

$$\frac{(hA)_1}{C_1} = 1.85\cdot 10^{-2}\ \mathrm{s^{-1}} \qquad \frac{(hA)_2}{C_2} = 2.97\cdot 10^{-4}\ \mathrm{s^{-1}}$$

$$(T_1 - T_2)_{st} = 19\ \mathrm{mK} \qquad (T_2 - T_c)_{st} = 2.51\ \mathrm{K}$$

The heat of the reaction can be calculated on the basis of the total temperature rise in the inner cell of the experiment[2]:

$$\Delta T = (T_m - T_0) = \frac{Q}{c_p} \cdot m_0 \tag{8}$$

Using the techniques outlined by White and Sturtevant[12, 13] the heat of the reaction is calculated using:

$$Q = \Delta T \cdot \frac{C_1 + C_{mat}}{V_1 \rho_1 m_0} \tag{9}$$

where C_1 and C_{mat} are the heat capacities of the liquid mixture and the materials (like sensors, etc.) in the inner cell, respectively. V_1 and ρ_1 are the reaction liquid volume and the mass density of the reaction liquid, respectively.

Calibrations performed with demineralized water (conductivity less than 2 μS cm^{-1}) gave for C_{mat}:

$C_{mat} = 71 \pm 12\ \mathrm{J\ K^{-1}}$

where the relatively large error merely results from the fact that the calibrations do not take into consideration the temperature dependence on the mass density and specific heat of water.

Because the volume of the inner cell is 163.0 ml, the heat capacity C_{mat} is about 10% of the total heat capacity of the inner cell.

Adiabatic experiments were always started with a temperature in the outer cell of about 2.51 K above that in the thermostatted bath. The advantage of this is a stable starting temperature. Because of the dynamic behaviour of the calorimeter, this temperature will not change for a considerable time. Owing to this the components may be mixed for a relatively long time before a noticeable deviation of adiabaticity is observed. In practice, mixing is completed within four seconds. The extra heat input by electrical energy is about 10% of the total heat generated in the outer cell.

2.4. *The practical operation*

For systems with completely unknown values of the kinetic constants, preliminary experiments are carried out in the simple Dewar reaction calorimeter described by Frankvoort and Dammers[2]. Considering the physical properties, like boiling point, the starting temperature is selected and thus the temperature of the thermostatted bath is fixed.

For the reaction system of the acid-catalyzed hydrolysis of methyl-oxirane (see section 3) the inner cell consists of a mixture of sulphuric acid and water with a concentration which is about eleven times that of the final reaction concentrations. The outer cell contains a mixture of water and methyl-oxirane with an acidity as neutral as possible to diminish the reaction between the constituents.

After temperature equilibration between the inner and outer cell the readings of the copper sensors on the ΔT versus T recorder are fixed on the control curve. When the temperature of the thermostatted bath is T_c the differences are

$T_2 = (T_c - 2.51)$ and $T_1 = (T_2 - 0.019)$.

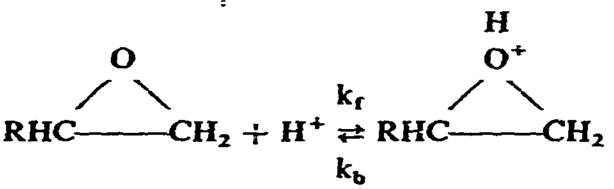
After putting on the data logging system the wall of the inner cell is opened, the cooling coil activated and the electrical heating set stand by. In three to four seconds complete mixing is established and the inner cell is closed. At the beginning of the reaction extra cooling is required. With rising temperature the cooling capacity is reduced as fast as possible and electrical heating is used to balance the conditions for adiabaticity in the inner cell. The control of the cooling coil as well as the electrical heat dissipation are carried out manually.

The data of an experiment written digitally on a cassette are transferred with a Silent 700 ASR-terminal to the CDC-cyber-73-28 digital computer system of SARA (Stichting Academisch Rekencentrum Amsterdam). Suitable computer programs[1-3] are available written in Algol-60.

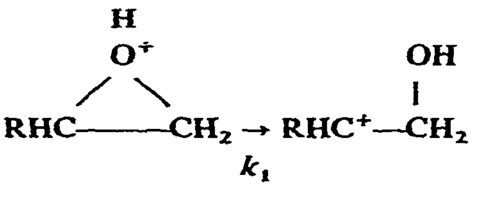
3. RESULTS AND DISCUSSION

The liquid phase reactions used to explore the properties of the adiabatic calorimeter are the acid catalyzed hydrolysis of methyloxirane (propylene oxide) into 1,2-propanediol (glycol) and of 2,3-epoxy-1-propanol into 1,2,3-propanetriol (glycerol).

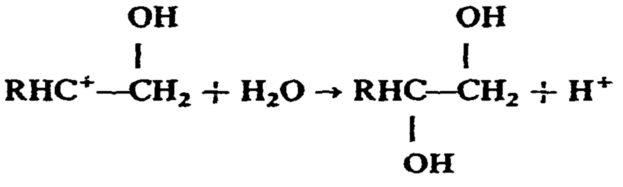
These moderately exothermic reactions with a heat of reaction of about 90 kJ mol^{-1} have been studied by several investigators[14-17]. Pritchard and Long[18,19] concluded that the most likely course for the hydrolysis is given by:



fast (10)



slow (11)



$$RHC^{+}(OH){-}CH_2 + H_2O \rightarrow RHC(OH){-}CH_2(OH) + H^{+}$$

fast (12)

where R is CH_3 or CH_2OH.

In a wide range of conditions with regard to the acidity and the water content of the reacting mixtures, the reaction rate is found to be of the first order in methyloxirane and proportional to the H^+ concentration.

The temperature-change determining step is given by eqn (11). The reaction rate equation is

$$r(m, T) = k_1\, m_c \qquad (13)$$

where m_c is the concentration of the conjugated acid of the epoxide. From eqn (10) the concentration m_c is calculated as

$$k_f\, m_{ox}\, m_{H^+} = k_b\, m_c \qquad (14)$$

where m_{ox} and m_{H^+} are the concentrations of epoxide and hydrogen ion, respectively. Substitution in eqn (13) and putting

$$k_2 = \frac{k_1\, k_f}{k_b} \qquad (15)$$

gives

$$r(m, T) = k_2\, m_{H^+}\, m_{ox} \qquad (16)$$

Equation (16) will be transformed in a modified Arrhenius equation with

$$k_2 = Z_2 \exp\left(\frac{-T_a}{T}\right) \qquad (17)$$

From thermodynamic calculations the enthalpy of the reaction of methyl-oxirane[20-23] (R = CH_3) is $\Delta H = -94.37$ kJ mol^{-1} and of 2,3-epoxy-1-propanol[20, 22, 24-26] (R = CH_2OH), $\Delta H = -88.83$ kJ mol^{-1}.

From the literature data the following values for the activation energy temperature T_a, the second-order frequency factor Z_2 and the second-order rate constant k_2 (at 298 K) are obtained.

	T_a (K)	Z_2 ($l\ mol^{-1}\ s^{-1}$)	k_2 (298 K) ($l\ mol^{-1}\ s^{-1}$)
methyl-oxirane[17]	9392	$2.12 \cdot 10^{12}$	0.044
2, 3-epoxy-1-propanol[14, 19]	8891	$3.64 \cdot 10^{10}$	0.0040

The calculations for 2,3-epoxy-1-propanol are based on two sets of data. The one at 273.15 K is from Pritchard and Long[19], the other from Brönsted et al.[14] was carried out at 293.15 K. Combination of these two sets and using eqn (14) result in the former mentioned values.

With the calorimeter described in section 2.1, a number of experiments have been conducted in which the hydrolysis of methyl-oxirane and 2,3-epoxy-1-propanol and the adiabaticity is controlled according to the procedures outlined in sections 2.3 and 2.4. The measured T, t relations are converted into dT/dt, T relations by means of the methods described by Frankvoort and Dammers[2].

All experiments have an initial reactant concentration of about 1.0 and 2.0

mol kg^{-1}, an initial temperature of about 279 K and a pH of about 1.0. The average values of T_a, Z_2 and of the second-order rate constants (298 K) are found to be:

	T_a (K)	Z_2 (kg mol^{-1} s^{-1})	k_2 (298 K) (kg mol^{-1} s^{-1})
methyl-oxirane	8932 ± 10	(1.33 ± 0.04) · 10^{12}	0.128 ± 0.002
2,3-epoxy-1-propanol	8827 ± 16	(8.5 ± 0.5) · 10^{10}	0.0118 ± 0.0007

The heats of reaction, Q, calculated with eqn (9) are for: methyl-oxirane: 93.6 ± 5.3 kJ mol^{-1} and for 2,3-epoxy-1-propanol: 88.2 ± 1.9 kJ mol^{-1}.

The calculations for methyl-oxirane could under some restriction be compared with the data of Pritchard and Long[17]. Their values are calculated from experiments carried out under isothermal conditions with initial concentrations of about 0.05 to 0.2 mol l^{-1}. In particular, the values for the frequency factor deviate considerably and thus also those for the reaction rate constant k_2.

The same remarks apply for the data obtained for experiments with 2,3-epoxy-1-propanol.

Comparing highly adiabatic with diathermic[3] experiments better agreement is found for the hydrolysis of methyl-oxirane. As extensively shown by Frankvoort[3] the values for T_a, Z_2 and k_2 (298K) determined by the diathermic method turned out to be: (8803 ± 28) K, (5.9 ± 1.4)10^{11} kg mol^{-1} s^{-1}, (0.089 ± 0.020) kg mol^{-1}s^{-1}, respectively.

To find a possible systematic error due to the method of calculating the kinetic constants from adiabatic experiments the integration method outlined by Frankvoort[3] is applied to the data from methyl-oxirane experiments. The results correspond very well to those calculated by the method mentioned before.

This indicates there is still an experimental bias between the isothermal (dilatometric) method used by Pritchard and Long, the diathermic method and the adiabatic method explained in this paper. Although in all cases the rate-determining step is eqn (11) and the heat evolution is connected to it, some experimental conditions will influence the results.

In the dilatometric experiments care should be taken regarding the uniformity and constancy of the temperature. The response time in the volume change reading may introduce a systematic error.

In diathermic experiments[3] systematic errors will occur from changes in the reactor ambient and fluctuations in the speed of stirring. These fluctuations result in changing values for the heat of stirring and heat transfer coefficient, used as known constants in the numerical calculations.

In adiabatic experiments the greatest error possible is a wrong power-control curve (see Fig. 4). This results in a systematic heat input to or heat withdrawal from the inner cell which results in a systematic higher respectively lower value for the heat of reaction. Comparing the results of the analysed reactions with the calculated enthalpy of reaction the determined reaction rate constants appear to be very useful.

ACKNOWLEDGEMENTS

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4. NOTATION

A	heat transfer surface area
c_p	average specific heat
C	heat capacity
h	overall heat transfer coefficient
ΔH	thermodynamically calculated enthalpy of reaction
k_n	pseudo reaction rate constant
m	molality of reaction solution
m_0	initial molality of reaction solution
Q	heat of reaction ($Q = -\Delta H$)
$r(m, T)$	reaction rate
t	time
T	absolute temperature of reacting mixture
T_a	activation-energy temperature
T_e	ambient temperature
T_m	maximum adiabatic reaction temperature
V	volume of reaction cell
W_q	external heat input
W_s	heat of stirring
Z	frequency factor in the Arrhenius equation
Z_n	modified frequency factor
ρ	mass density

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