

DERIVATION OF KINETIC CONSTANTS OF SIMPLE REACTIONS BY MEANS OF ADIABATIC REACTION CALORIMETRY

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ABSTRACT

The present paper is concerned with experimental techniques for conducting accurate temperature-time measurements in a semi-adiabatic reaction calorimeter. In addition, mathematical methods are presented which make it possible to derive reliable values for the activation energy and the frequency factor from the observed temperature-time relation.

1 INTRODUCTION

In a previous paper¹ we discussed a simple method to obtain the activation energy E and frequency factor Z of chemical reactions from an analysis of the temperature-time curve observed in adiabatic batch experiments. The method in question applies to cases in which the reaction rate can be represented by an expression of the type

$$U(c, T) = Zc^n \exp\left(-\frac{T_2}{T}\right) \quad (1)$$

where $T_2 = \frac{E}{R}$

In perfectly adiabatic systems the rate of temperature change then is given by the non-linear differential equation

$$\frac{dT}{dt} = Z_n(T_m - T)^n \exp\left(-\frac{T_2}{T}\right) \quad (2)$$

satisfying the initial and final conditions

$$\begin{aligned} t = 0; & \quad c = c_0; & \quad T = T_0 \\ t = \infty; & \quad c = 0; & \quad T = T_m = T_0 + \frac{Q}{c_p} c_0 \end{aligned} \quad (3a)$$

while Z_n is a modified frequency factor:

$$Z_n = Z \left(\frac{c_p}{Q} \right)^{n-1} = Z \left(\frac{c_0}{T_m - T_0} \right)^{n-1} \quad (3b)$$

Equation (2) can be transformed into an Arrhenius-type relation

$$\ln k_n = \ln \frac{dT}{dt} - n \ln (T_m - T) = \ln Z_n - \frac{T_2}{T} \quad (4a)$$

$$\text{where } k_n = \frac{\frac{dT}{dt}}{(T_m - T)^n} \quad (4b)$$

is a pseudo reaction rate constant. From the linear relation between $\ln k_n$ and $1/T$, the kinetic constants Z_n and T_2 can be evaluated. A typical example is presented in Fig. 3 of our previous paper¹, relating to the homogeneous decomposition of hydrogen peroxide in acid solution². The modified Arrhenius plot shown in this graph is based on measurements conducted in a simple Dewar calorimeter^{3,4}.

Apart from the restrictive assumptions introduced in the derivation of the differential eqn (2), the applicability of the above method largely depends on the availability of a reliable value for the maximum adiabatic reaction temperature T_m and on the possibility of deriving accurate dT/dt values from the experimental T, t curve. The effect of T_m on the shape of the modified Arrhenius plot is clearly illustrated in Fig. 1, where the straight line represents the relation between $\ln k_n$ and $1/T$ for a first-order reaction ($n = 1$) with $T_2 = 9000$ K and $Z_1 = 5.0 \times 10^{11} \text{ sec}^{-1}$. With these values of n , T_2 and Z_1 , and with $T_m = 300$ K, we can calculate from eqn (2) a series of dT/dt , T values to simulate a set of experimental data. Taking these dT/dt , T values, but using T_m values which differ slightly from 300 K, the values of $\ln k_1$ calculated from eqn (4b) are found to deviate considerably from the straight line. In Fig. 1 the upper and lower curve represent the variation of $\ln k_1$ with $1/T$ for $T_m = 299.8$ and 300.2 K, respectively. Naturally, a linear fit of these curves in the temperature range between 280 and 298.5 K would lead to erroneous values for the kinetic constants:

T_m (K)	T_2 (K)	Z_1 (sec^{-1})	σ
299.8	9771.3	7.52×10^{12}	5×10^{-3}
300.0	9000.0	5.00×10^{11}	—
300.2	8365.8	5.37×10^{10}	4×10^{-3}

This example indicates that the uncertainty in T_m —and, consequently, in the temperature measurements—should preferably be less than 0.01 K in order to obtain satisfactory results from the modified Arrhenius plot. The same conclusion is reached with regard to the calculation of dT/dt values. The subsequent sections are therefore

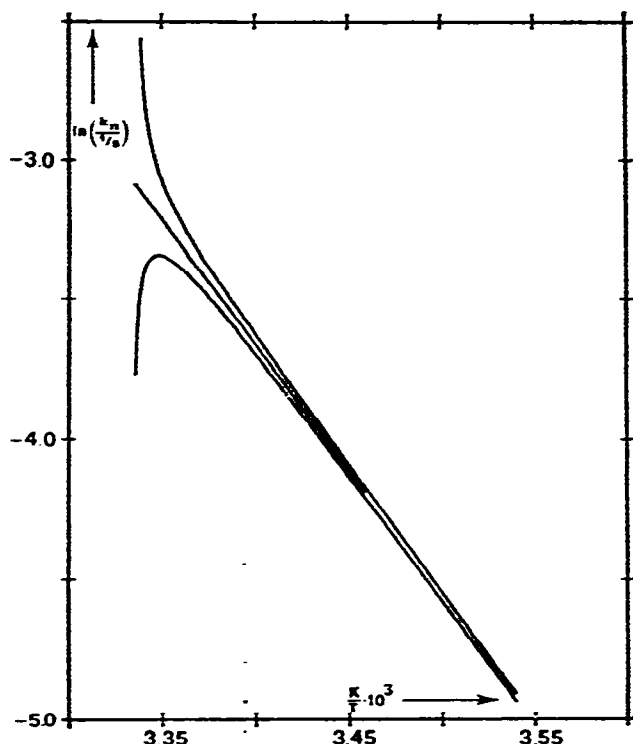


Fig. 1. The effect of T_m on the shape of the modified Arrhenius plot (upper curve: $T_m = 299.8$ K; middle curve: $T_m = 300.0$ K; lower curve: $T_m = 300.2$ K).

mainly concerned with experimental means to improve the accuracy of the temperature measurements and with mathematical techniques to derive reliable values of T_a and Z_n from the observed T, t curve. In addition, two different methods are suggested to obtain accurate results from essentially non-adiabatic measurements.

2 EXPERIMENTAL

2.1 The model reaction

The liquid-phase model reaction used to explore the properties of the reaction calorimeter is the acid-catalyzed conversion of methyloxirane (propylene oxide) into propanediol (propylene glycol):



This moderately exothermic hydrolysis reaction ($\Delta H = -89.18 \text{ kJ mol}^{-1}$ (refs. 5–8)) has been studied by several investigators^{9–11}. Values for the activation energy and the frequency factor have been reported by Long and Pritchard^{12–14} (for aqueous solutions) and by Furusawa et al.¹⁵ (for mixtures of water and methanol).

In a wide range of conditions with regard to the acidity and the water content of the reacting mixture, the reaction rate is found to be of the first order in methyl-oxirane (MO), proportional to the H^+ concentration and independent of the H_2O concentration:

$$U = -\frac{d(MO)}{dt} = k_1(MO) = k_2(H^+)(MO); \quad k_1 = k_2(H^+) \quad (6)$$

$$k_1 = Z_1 \exp\left(-\frac{T_a}{T}\right); \quad k_2 = Z_2 \exp\left(-\frac{T_a}{T}\right); \quad Z_1 = Z_2(H^+)$$

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 25°C) are obtained:

	T_a (K)	Z_2 (l mol ⁻¹ sec ⁻¹)	k_2 (l mol ⁻¹ sec ⁻¹)
Long and Pritchard ¹²⁻¹⁴	9370	1.99×10^{12}	4.47×10^{-2}
Furusawa et al. ¹⁵	9060	3.30×10^{11}	2.10×10^{-2}

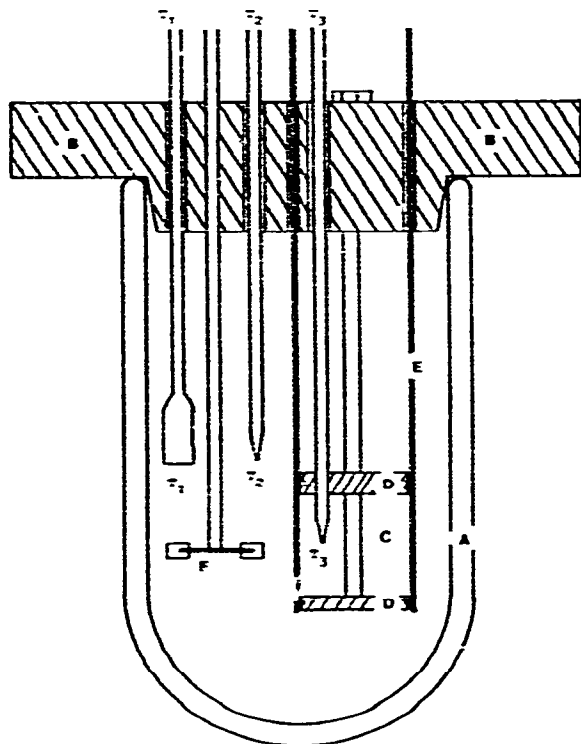


Fig. 2. The calorimeter assembly.

2.2 The reaction calorimeter

The reaction calorimeter (Fig. 2) used for the present measurements is a modified version of the apparatus described by Pritchard and Skinner³. The calorimeter consists of a 1.5-l dewar vessel A, provided with perspex baffles, a thermocoax heating coil for calibration purposes, a pH-electrode and a perforated perspex cover B. The dewar is immersed in a thermostatic bath, the temperature (T_c) of which can be kept constant within 0.01 K.

The dewar is partially filled with an aqueous solution of methyloxirane, while a solution of sulfuric acid is contained in compartment C of a cylindrical tube and enclosed by two teflon pistons D. The pistons are kept in place by a piston-rod, which is firmly attached to the perspex cover, while wall E of the tube can be moved up and down. By lifting this wall, the acid solution rapidly flows into the methyloxirane solution; further mixing is achieved by means of a flat-blade turbo-stirrer F (1500 rpm).

The temperature of the reacting mixture is recorded digitally at equidistant times by means of a Hewlett-Packard quartz-thermometer T_1 (calibrated within 0.001 K at the Netherlands Service of Metrology, The Hague) with an HP-2580-D sensor. This instrument determines the time-averaged temperature of the reaction mixture in each of the successive time intervals. The accuracy of the temperature measurements depends on the length of the intervals selected for the reaction system under consideration; it may vary from 0.01 K (for intervals of 0.1 sec) to 0.0001 K (for intervals of 10 sec). Most measurements have been conducted with the 0.001 mode. Temperature sensors T_2 and T_3 are diodes, developed in our institute, which serve to check the temperature difference between the separated solutions before starting the reaction; the accuracy of these sensors is of the order of 0.01 K.

The calculation of the kinetic constants T_n and Z_n from relation (4a) is based on the assumption that the chemical reaction is the only heat source or sink. However, a more realistic heat balance for the reaction calorimeter sketched in Fig. 2 should also involve the production of heat by stirring and the exchange of heat between the calorimeter and its surroundings:

$$c_p \frac{dT}{dt} = QU + W_s - hA(T - T_c) \quad (7)$$

The magnitude of the last two terms in eqn (7) has been estimated from the variation of T with t in non-reacting systems. The heat balance then reduces to

$$\frac{dT}{dt} = \frac{W_s}{c_p} - \frac{hA}{c_p}(T - T_c) \quad (8)$$

and the quantities W_s/c_p and hA/c_p can thus be obtained from the linear relation between dT/dt and $T - T_c$. The average values from 18 measurements were found to be

$$W_s/c_p = (4.3 \pm 0.5) \times 10^{-4} \text{ K sec}^{-1} \quad (9)$$

$$hA/c_p = (1.7 \pm 0.3) \times 10^{-5} \text{ sec}^{-1}$$

Since the average rate of temperature rise due to chemical reaction is of the order of 0.03 K sec^{-1} , we conclude that the "non-adiabatic" terms in eqn (7) represent relatively small effects. In the final part of the T, t curve, however, they may become of importance because of the decreasing reaction rate. The ultimate effect of these terms on the values obtained for T_n and Z_n will be illustrated in Section 3 by means of computer calculations simulating actual experiments.

2.3 Numerical estimation of temperature derivatives

The calculation of T_n and Z_n via eqn (4a) and of W_s/c_p and hA/c_p via eqn (8) requires accurate values for dT/dt as a function T . For the present purpose the classical methods for the numerical calculation of derivatives (Newton, Stirling¹⁶) are not particularly suitable. With these methods, even minor uncertainties in the measured T, t relation may give rise to unacceptably large errors in the calculated dT/dt values¹⁷; in fact, a loss of two or three significant figures is not unusual.

We therefore preferred to use the so-called method of splines^{18,19}, which is based on the following procedure. Let us consider a series of successive temperatures $T_1, T_2, T_3, \dots, T_n$ measured at (equidistant) times $t_1, t_2, t_3, \dots, t_n$. Within each of the successive intervals we now assume that the reactor temperature varies as a function of time according to

$$T(t) = a_0 + a_1 t + a_2 t^2 + a_3 t^3 \quad (10a)$$

with

$$\frac{dT}{dt} = a_1 + 2a_2 t + 3a_3 t^2 \quad \text{and} \quad \frac{d^2T}{dt^2} = 2a_2 + 6a_3 t \quad (10b)$$

For each of the time intervals the coefficients in eqn (10a) are determined by the conditions that function $T(t)$ as well as its first and second derivatives must be continuous at the transition of successive intervals. By means of a recursive procedure one then obtains a smoothly varying function, which covers the entire temperature range from T_1 to T_n and provides accurate values for the first and second derivatives at any point of the T, t curve.

Reinsch²⁰ applied the method of splines to input data subject to random errors. The algorithm developed by this author is used in our present calculations and results in a narrow band (rather than a single curve) for dT/dt as a function of T . Starting from input data with a relative error of about 10^{-5} (and corrected for the relatively slow response and the slight non-linearity of the quartz temperature sensor), the accuracy of the derivatives is found to be about 10^{-4} . The calculations were carried out on the CDC-cyber-73-28 digital computer at SARA (Stichting Academisch Rekencentrum Amsterdam), using an Algol-50 programme.

3 ADIABATIC TREATMENT OF NON-ADIABATIC DATA

In Section 2.2 we observed that the reaction calorimeter used for our measure-

ments is not a perfectly adiabatic system. The calculation of T_s and Z_n , on the other hand, is based on the validity of eqn (4a), in which terms like W_s and $hA(T-T_c)$ have not been taken into consideration. We must therefore investigate as to how far the values of the quantities T_s and Z_n are affected by the use of essentially non-adiabatic data in conjunction with a strictly adiabatic model. To this end we assign realistic values to the parameters in the coupled differential equations

$$\frac{dT}{dt} = -\frac{Q}{c_p} \frac{dc}{dt} + \frac{W_s}{c_p} - \frac{hA}{c_p}(T-T_c) \quad \text{and} \quad \frac{dc}{dt} = -Z_1 c \exp\left(-\frac{T_s}{T}\right) \quad (11)$$

which represent the behaviour of the reaction calorimeter described in Section 2.2 for an irreversible first-order reaction. These non-linear equations are then integrated numerically with the aid of a standard Runge-Kutta programme²¹. The T, t relation obtained in this way can be subjected to random noise and used to simulate a set of experimental data.

From these non-adiabatic data we now recalculate the kinetic constants T_s and Z_1 according to the methods outlined in the preceding sections, which implies the applicability of "adiabatic" eqn (4a). For "experimental" data based on the parameter values:

$$\begin{aligned} T_s &= 9.100 \times 10^3 \text{ K} & Q/c_p &= 1.833 \times 10^1 \text{ kg K mol}^{-1} \\ Z_1 &= 1.650 \times 10^{11} \text{ sec}^{-1} & W_s/c_p &= 4.300 \times 10^{-5} \text{ K sec}^{-1} \\ & & hA/c_p &= 5.000 \times 10^{-5} \text{ sec}^{-1} \end{aligned} \quad (12a)$$

we find from adiabatic fits at two different initial concentrations:

$$\begin{aligned} T_0 &= 278 \text{ K} & T_0 &= 278 \text{ K} \\ c_0 &= 1.0 \text{ mol l}^{-1} & c_0 &= 2.0 \text{ mol l}^{-1} \\ T_s &= 8.93 \times 10^3 \text{ K} & T_s &= 9.17 \times 10^3 \text{ K} \\ Z_1 &= 0.92 \times 10^{11} \text{ sec}^{-1} & Z_1 &= 2.22 \times 10^{11} \text{ sec}^{-1} \end{aligned} \quad (12b)$$

An analysis of these results indicates that the discrepancy between the "adiabatic" values in (12b) mainly originates from the difference in reaction time. At the lower initial concentration it takes much more time to attain essentially complete conversion than at the higher initial concentration. Since the relative importance of the two smaller terms in eqn (11) varies in the course of the reaction, it is clear that the combined effect of these terms on T_s and Z_1 will depend on the total length of the reaction time.

This difficulty might be overcome 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 heat transfer to a cooling medium of variable temperature:

$$W_s - hA(T-T_c) = 0 \quad \text{or} \quad T(t) - T_c(t) = \frac{W_s}{hA} = \text{constant} \quad (13)$$

A reaction calorimeter designed to operate with a constant temperature difference between the reacting mixture and the cooling medium is now being tested. The results obtained with this quasi-adiabatic apparatus will be reported in a forthcoming publication.

It should be noted, however, that the values of T_m in (12b) differ from the correct value in (12a) by less than 2%. With the presently available equipment and techniques for data processing, the adiabatic treatment of non-adiabatic data thus leads to the same degree of accuracy as obtained with the conventional isothermal methods.

4 NON-LINEAR REGRESSION PROCEDURE

The tremendous effect of the T_m values on the shape of the modified Arrhenius plot made it desirable to investigate the applicability of more sophisticated regression methods, which provide reliable values for T_a and Z_n as well as for T_m . One such method is based on the logarithmic form of the differential eqn (2), viz.

$$\ln \frac{dT}{dt} = \ln Z_n + n \ln (T_m - T) - \frac{T_a}{T} \quad (14)$$

or

$$y = A + n \ln (B - x_1) - Cx_2 \quad (15a)$$

where

$$\begin{aligned} y &= \ln \frac{dT}{dt} & A &= \ln Z_n = \ln Z + (n-1) \ln \frac{c_p}{Q} \\ x_1 &= T & B &= T_m \\ x_2 &= \frac{1000}{T} & C &= \frac{T_a}{1000} \end{aligned} \quad (15b)$$

According to the least squares method, the most appropriate values of the parameters A, B and C must satisfy the condition

$$f(A, B, C) = \sum \{y - A - n \ln (B - x_1) + Cx_2\}^2 = \text{minimal} \quad (16)$$

resulting in the normal equations

$$\sum y - pA - n \sum \ln (B - x_1) + C \sum x_2 = 0 \quad (17a)$$

$$\sum \frac{y}{B - x_1} - A \sum \frac{1}{B - x_1} - n \sum \frac{\ln (B - x_1)}{B - x_1} + C \sum \frac{x_2}{B - x_1} = 0 \quad (17b)$$

$$\sum x_2 y - A \sum x_2 - n \sum x_2 \ln (B - x_1) + C \sum x_2^2 = 0 \quad (17c)$$

where the summation is carried out over the number of observations (experimental

points) p . This system of three equations with three unknowns (viz. A, B and C) may be solved via a three-dimensional Newton-Raphson iteration procedure, which requires adequate starting values for the parameters $\ln Z_n$, T_a and T_m . Since sufficiently accurate starting values for $\ln Z_n$ and T_a may not be available, it seems reasonable to take advantage of the fact that the normal equations are linear in A and C. Thus, from (17a) and (17c), the quantities A and C can be expressed as functions of B:

$$\begin{aligned} A &= a + b_1 \sum \ln(B - x_1) - b_2 \sum x_2 \ln(B - x_1) \\ C &= c + b_2 \sum \ln(B - x_1) - b_3 \sum x_2 \ln(B - x_1) \end{aligned} \quad (18a)$$

where

$$\begin{aligned} a &= \frac{(\sum x_2)(\sum x_2 y) - (\sum x_2^2)(\sum y)}{(\sum x_2)^2 - p \sum x_2^2}; & c &= \frac{p \sum x_2 y - (\sum x_2)(\sum y)}{(\sum x_2)^2 - p \sum x_2^2} \\ b_1 &= \frac{n \sum x_2^2}{(\sum x_2)^2 - p \sum x_2^2}; & b_2 &= \frac{n \sum x_2}{(\sum x_2)^2 - p \sum x_2^2}; & b_3 &= \frac{np}{(\sum x_2)^2 - p \sum x_2^2} \end{aligned} \quad (18b)$$

For a given set of experimental T , t values (and calculated dT/dt , T values) the quantities a , c , b_1 , b_2 and b_3 are constants, which can be obtained from the measured temperature-time relation. On substituting (18a) in (17b) we find:

$$\begin{aligned} f(B) &= \sum \frac{y}{B - x_1} - n \sum \frac{\ln(B - x_1)}{B - x_1} - a \sum \frac{1}{B - x_1} + c \sum \frac{x_2}{B - x_1} - \\ &- b_1 \left(\sum \frac{1}{B - x_1} \right) \sum \ln(B - x_1) + b_2 \left(\sum \frac{x_2}{B - x_1} \right) \sum \ln(B - x_1) + \\ &+ b_2 \left(\sum \frac{1}{B - x_1} \right) \sum x_2 \ln(B - x_1) - b_3 \left(\sum \frac{x_2}{B - x_1} \right) \sum x_2 \ln(B - x_1) = 0 \end{aligned} \quad (19)$$

The problem has now been reduced to a single non-linear equation in B, which can be solved by means of a one-dimensional Newton-Raphson procedure:

$$B_i = B_{i-1} + \delta B_i \quad \text{with} \quad i = 1, 2, 3, \dots$$

and

$$f(B_i) \simeq f(B_{i-1}) + f'(B_{i-1}) \cdot \delta B_i = 0, \quad \text{where} \quad \delta B_i = - \frac{f(B_{i-1})}{f'(B_{i-1})}$$

In order to obtain rapid convergence of successive δB values, an acceptable starting value (B_0) should be available. Since T_m is the limiting reaction temperature for $t \rightarrow \infty$, the T_m value estimated by direct extrapolation of the experimental T , t curve

may not be sufficiently accurate. In that case a reliable starting value for B_0 can be obtained in the following way.

At reaction temperatures in the vicinity of T_m , the reaction rate depends almost entirely on the vanishing reactant concentration, whereas the temperature dependence is no longer of importance. Sufficiently close to T_m , we may therefore replace eqn (2) by the simpler expression

$$\frac{dT}{dt} \simeq Z_n (T_m - T)^n \exp\left(-\frac{T_a}{T_m}\right) = k_m (T_m - T)^n \quad \text{for} \quad T \simeq T_m \quad (20a)$$

where

$$k_m = Z_n \exp\left(-\frac{T_a}{T_m}\right) \quad (20b)$$

is the limiting value of rate constant k_n for $T \rightarrow T_m$. From eqn (20a) we observe that the final part of the $dT/dt, T$ curve can be represented by a straight line for $n = 1$ (first-order reaction) and by a parabola for $n = 2$ (second-order reaction). An example of the applicability of approximation (20a) is shown in Fig. 3 derived from the final part of a T, t curve for the adiabatic hydrolysis of methyloxirane in acid solution.

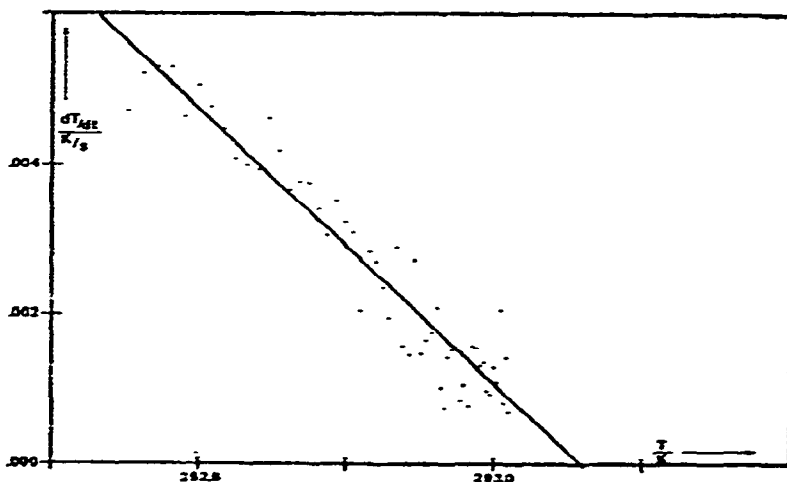


Fig. 3. The approximation of T_m by eqn (20a); the fitted value for T_m is 293.118 K, while the regression procedure in eqn (19) gives 293.120 K.

RESULTS AND DISCUSSION

With the reaction calorimeter described in Section 2.2 a number of experiments have been conducted in which the hydrolysis of methyloxirane (Section 2.1) served as the model reaction. The measured T, t relations were converted into $dT/dt, T$ relations by means of the methods mentioned in Section 2.3 and the latter data were then subjected to the regression procedure outlined in Section 4. From two sets of 15

experiments with an initial temperature of about 278 K, a pH of about 1.0 and initial reactant concentrations of about 1.0 and 2.0 mol l⁻¹, respectively, the average values of T_a and Z_2 and of the second-order rate constant k_2 are found to be:

	c_0 (mol l ⁻¹)	T_a (K)	$Z_2 \times 10^{-12}$ (l mol ⁻¹ sec ⁻¹)	k_2 (25°C) (l mol ⁻¹ sec ⁻¹)
set I	1.0	8926 ± 42	1.02 ± 0.30	0.102 ± 0.016
set II	2.0	9167 ± 37	1.56 ± 0.40	0.069 ± 0.009

In view of the high reactant concentrations involved, the accuracy of the results at one given initial concentration is quite satisfactory. As already noticed in Section 3, however, the discrepancy between the values of T_a and Z_2 at different initial concentrations constitutes a serious limitation of the adiabatic treatment of non-adiabatic data. This limitation becomes more severe if the final part of the T, t is completely included in the set of experimental data.

A possible experimental solution of this problem has already been suggested in Section 3. Meanwhile, we are also working on a mathematical treatment, which is based on the complete differential eqns (11). Introducing acceptable starting values for the parameters in (12a), one can integrate these equations numerically and determine the sum of the squares of the differences between the experimental and the calculated reaction temperatures at a given set of t values. By means of a suitable iterative procedure, an improved set of parameter values is then obtained and with these values one again integrates eqns (11) and determines the sum of squares. This procedure is continued until the sum of squares attains its minimum value. A computer programme performing these calculations is presently being tested.

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NOMENCLATURE

- A heat-transfer surface area
- c concentration of key-reactant
- c_0 initial concentration of key-reactant
- c_p average volumetric heat capacity
- E energy of activation
- h overall heat-transfer coefficient
- k_m pseudo reaction rate constant near T_m , eqn (20b)
- k_n pseudo reaction rate constant, eqn (4a)

n	reaction order
Q	heat of reaction (positive for exothermic reactions)
R	gas constant
t	time
T	absolute temperature of reacting mixture
T_0	initial temperature of reacting mixture
T_a	activation-energy temperature, eqn (1)
T_c	ambient temperature
T_m	maximum adiabatic reaction temperature, eqn (3a)
U	reaction rate
W_s	heat of stirring
Z	frequency factor, eqn (1)
Z_m	modified frequency factor, eqn (3b)
σ	standard deviation

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