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DTA CURVES AND NON-ISOTHERMAL REACTION RATES

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ABSTRACT

Differential thermal analysis (DTA) is an effective means for studying chemical reactions, but its application to reaction kinetics is handicapped by the involvement of temperature feedback from the reaction heat and by the solvent dependence of the thermal conductivity.

General, empirical relationships are derived from digital computer application which allow to transform half width and shape index of a DTA curve of any first-order process in a uniformly temperated sample to the values of the corresponding rate curve at linearly increased temperature.

The expressions are complemented by some new relationships for an n-order reaction and are useful for the kinetic study of complex processes.

1. INTRODUCTION

Since most of the real reactions in chemistry are complex, we have searched for adequate criteria to draw conclusions from DTA and/or rate curves for the reaction mechanisms involved. From analog computer simulations and DTA experiments with reactions in solution, one of us had stated[1–5] that the shape index S of a rate curve at linearly increasing temperature, together with the half width h (referred to the activation parameters of the initiating reaction) are such values which characterize broadness and asymmetry of a DTA curve and are readily available.

DTA signals of reactions in solution may be seen as modified non-isothermal reaction rates if the construction of the apparatus allows the temperature difference, Θ, observed between the reacting solution and the reference solution, to be described by the use of the calorimetric equation[6–8].

$$\frac{\mathrm{d}\Theta}{\mathrm{d}t} = \frac{V}{C_p}\frac{\mathrm{d}q}{\mathrm{d}t} - c\Theta = \frac{V}{C_p}\Delta H v - c\Theta \tag{1}$$

V = volume of the sample (and reference)
C_p = heat capacity of the sample
$\mathrm{d}q/\mathrm{d}t$ = heat flow generated by the reaction
ΔH = reaction enthalpy (kcal mol^{-1})
c = "kinetic" cell constant (min^{-1})
v = reaction rate

The fundamental study of the signals of complex reactions requires elimination of the "kinetics" of heat conduction, i.e., transformation of the "delayed" DTA curves to the real rate curves.

The direct way to do this is the instantaneous calculation of the reaction rate (which is proportional to the heat flow) from the temperature difference recorded in a DTA experiment via eqn (1). The purpose of this paper, however, is to demonstrate that also a determination of the shape index S_{ideal} and half width h_{ideal} of the rate curve is possible from the values S and h observed.

It is clear that the cell constant c as well as the deviation from temperature linearity with time caused by the reaction heat must intrude into such an attempt. Furthermore, it will be shown that it is possible to use a unique quantity which summarizes the influences of the reaction data, namely the Arrhenius activation energy and the frequency factor, as well as the heating rate chosen.

2. A UNIQUE KINETIC PARAMETER

The rate of a first-order reaction at a constant heating rate m is given by the time law[9]

$$v(t) = -\frac{\mathrm{d}[A]}{\mathrm{d}t} = [A]_0 k(t) \mathrm{e}^{-\int k(t)\mathrm{d}t} \tag{2}$$

where k is represented by the Arrhenius equation

$$k(t) = k_\infty \mathrm{e}^{-E/RT} = k_\infty \mathrm{e}^{-E/mRt} \tag{3}$$

(E = activation energy; k_∞ = frequency factor min^{-1}; R = gas constant; T = temperature in K; t = time in min; m = heating rate) if the time t ($= T/m$) is considered from absolute zero temperature.

If we introduce another time-dependent variable u

$$\int k\mathrm{d}t = u(t)k \tag{4}$$

we obtain

$$\frac{\mathrm{d}\int k\mathrm{d}t}{\mathrm{d}t} = \frac{\mathrm{d}(uk)}{\mathrm{d}t} = \frac{\mathrm{d}u}{\mathrm{d}t}k + u\frac{\mathrm{d}k}{\mathrm{d}t} = \left(\frac{\mathrm{d}u}{\mathrm{d}t} + u\frac{E}{mRt^2}\right)k \tag{5}$$

but on the other hand

$$\frac{\mathrm{d}\int k\mathrm{d}t}{\mathrm{d}t} = k \tag{6}$$

The conditions are much simplified if we only consider very high frequency factors so that

$$\ln k_\infty \gg 2 \tag{7}$$

since in this case u is given by the following equation[9,12–14]

$$u = \frac{R}{mE} T^2 = \frac{mR}{E} t^2 \tag{8}$$

Equalization of both expressions for $\mathrm{d}\int k\,\mathrm{d}t/\mathrm{d}t$ (eqns (5) and (6)) then yields the relationship

$$k = \left(1 + \frac{\mathrm{d}u}{\mathrm{d}t}\right) k \tag{9}$$

Consequently, $\mathrm{d}u/\mathrm{d}t = 0$, i.e., if condition (7) is fulfilled, a constant value has to be taken for u. Since, in addition,

$$\frac{\mathrm{d}v}{\mathrm{d}t} = [A]_0 \left(\frac{E}{mRt^2} - k\right) k\,\mathrm{e}^{-uk} = [A]_0 \left(\frac{1}{u(t)} - k\right) k\,\mathrm{e}^{-uk} \tag{10}$$

then the following simple relationships are obtained for the important quantities of a non-isothermal rate curve[10]:

rate constant at the maximum $k_m = \dfrac{1}{u}$ (11)

temperature at the maximum $T_m = \dfrac{E/R}{\ln k_\infty + \ln u}$ (12)

maximum rate $v_m = \dfrac{[A]_0}{u \cdot e}$ (13)

According to eqns (8), (3) and (11), the constant u is accessible from the activation parameters by numerical regression *via* eqn (14):

$$u = \frac{E}{mR\,(\ln k_\infty + \ln u)^2} \tag{14}$$

If we consider the half values of v_m, eqn (15) is obtained

$$\frac{[A]_0}{2eu} = [A]_0 k\,\mathrm{e}^{-uk} \tag{15}$$

or

$$(uk)_{1,2} = \ln (uk)_{1,2} + 1 + \ln 2 \tag{16}$$

This equation represents the intersection of a straight line with a logarithmic curve showing two solutions $(uk)_1$ and $(uk)_2$. Numerical evaluation with the iterative program Stud 14 A for the Hewlett-Packard calculator HP-65 shows that

$$\ln (k_2/k_1) = 2.42. \tag{17}$$

Thus, eqn (16) is responsible for the surprising phenomenon that for the half width of a DTA curve of any first-order process for a constant, relatively high cell constant

($c > 0.14$) the following unique relationship is valid,

$$\frac{E}{h(\log k_\infty - \log k_m)^2} = \frac{Rum}{h \cdot (\log e)^2} = \frac{R(\ln 10)^2}{\ln k_2/k_1} = 0.0047 = M_1 \text{ kcal mol}^{-1}\text{ K}^{-1} \tag{18}$$

which may directly be derived from the Arrhenius eqn (3) for temperatures T_1 and T_2[1,2].

The experimental evidence for eqn (18) was astonishing, since, in many examples, it is not clear whether the assumption (7) is fulfilled satisfactorily. To confirm the usefulness of the concept of using a constant u also for reactions with low frequency factors, we developed computer programs for stepwise regression, primarily for the pocket calculator Hewlett-Packard HP-65[15], and controlled the validity of the fundamental and useful expressions (13) and (18) for twenty hyphothetical calibration reactions with activation energies 1-50 kcal mol^{-1} and frequency factors 10^4–10^{30} min^{-1}.

As can be seen in Table 1, the following general relationships hold, cf. eqn (13)

$$\frac{v_m}{[A]_0} u_m = 0.410 \pm 0.008 \approx \frac{1}{e} \tag{19}$$

and

$$\frac{h}{mu_m} = 2.252 \pm 0.064 = \frac{R}{M_1}(\ln 10)^2 = \ln\frac{k_2}{k_1} \tag{20}$$

(standard deviation)

(cf. eqns (17) and (18)).

Hence, it is obvious that u_m, the u-value at the maximum, is indeed a very useful parameter in non-isothermal reaction kinetics. Analogous to the rate constant in the isothermal case, the product $u \cdot m$, for unit rate constant, is a reaction-specific quantity which could be denoted as "specific temperature difference".

In the general case of a reaction of order $n \geq 1$, for $[A]_0 = 1$ mol l^{-1} we have found by computer simulations that

$$\frac{h}{mu_m} = 2.25\, n^{0.52 \pm 0.03} \tag{21}$$

(cf. eqn (20)).

3. THE SHAPE INDEX

The shape index of a non-isothermal rate curve describes the ratio of the slopes of both tangents at the points of inflection. As is shown in Table 1, this value remains remarkably constant for any first-order process. We obtained

$$S_\infty = 0.55 \pm 0.03 \text{ (standard deviation)} \tag{22}$$

for the 20 reactions studied (cf. eqn (34)).

TABLE 1

SOME DATA AND EXPRESSIONS FROM NON-ISOTHERMAL RATE CURVES OF A FIRST-ORDER REACTION (HP-65 SIMULATIONS)

E = activation energy, kcal mol^{-1}; k_∞ = frequency factor, min^{-1}; u_m = see text, min; c_m = maximum signal height, mol dm^{-3} min^{-1}. Simulation conditions: cf. (ref. 15); $m = 1.5$ K min^{-1}, $[A]_0 =$ 1 mol dm^{-3} no feedback.

Reaction No.	u_m	E	$\log k_\infty$	$c_m \cdot u_m$	h/mu_m	S
1	0.46	1	12	0.418	2.17	0.60
2	0.88	2	12	0.406	2.22	0.55
3	1.63	6	15	0.410	2.36	0.57
4	2.28	15	20	0.414	2.30	0.57
5	2.46	6	12	0.414	2.26	0.53
6	3.88	15	15	0.406	2.20	0.53
7	3.96	10	12	0.400	2.32	0.54
8	4.45	30	20	0.394	2.26	0.52
9	5.79	15	12	0.404	2.30	0.54
10	5.78	20	14	0.404	2.26	0.54
11	6.20	6	7	0.414	2.37	0.57
12	8.05	8	7	0.412	2.29	0.58
13	10.05	4	4	0.400	2.21	0.63
14	11.05	30	20	0.400	2.26	0.55
15	14.21	6	4	0.426	2.20	0.60
16	15.09	30	10	0.400	2.25	0.56
17	17.90	50	12	0.402	2.35	0.55
18	17.93	15	6	0.420	2.20	0.59
19	23.27	15	5	0.424	2.15	0.62
20	33.33	30	6	0.418	2.21	0.58

On the other hand, the following empirical relationship (which was checked for $0.1 < n < 10$(!), $[A]_0 = 1$ and $u = 6$), is valid for the shape index:

$$S \approx \frac{n^2}{n^2 + a}\,[S_\infty(1+a) + b(n-1)] \tag{23}$$

(a and b are constants; see Table 2) which includes the results of Kissinger[16] for low n-values

$$S \approx 0.63\, n^2 \tag{24}$$

and the results of our analog simulations at orders 1 and 2[1,2] (Table 2). Other reactions for unit initial concentrations and sufficiently high frequency factors also obey eqn (23).

In conclusion, the shape index S and the M-index ("reaction-type index" which is derived from h) are values independent of the activation data, but characteristic of the reaction order.

TABLE 2

SHAPE INDEX OF A NON-ISOTHERMAL RATE CURVE OF ORDER n

Constants in eqn (23): $a = 1.59$ $b = 0.21$ $S_\infty = 0.55$.

n	*S value*		*Computer*
	eqn (24) (*Kissinger*)	*eqn* (23) (*Koch*)	
0.05	0.0016	0.0019	—
0.1	0.0063	0.0077	—
0.2	0.025	0.031	—
0.4	0.101	0.119	—
0.6	0.227	0.247	0.252
0.8	0.403	0.397	0.420
1	0.630	0.550	0.551
1.5	(1.42)	0.896	0.861
2	(2.52)	1.17	1.12
2.5	(3.93)	1.39	1.32
3	(5.67)	1.57	1.49
4	(10.05)	1.87	1.85
6	(22.68)	2.37	2.15
8	(40.32)	2.82	2.66
10	(63.0)	3.26	3.15

4. FIRST-ORDER DTA CURVES

(*a*) *Half width*

Apart from the HP-65 programs for the determination of shape index and half width of model DTA curves whose application is relatively time-consuming*, programs for the Mulheim computer centrum[17] were developed. The simulation of the DTA curves was based on the same twenty reactions as in Table 1, using $m = 1.5$ K min^{-1} and the following scale of c-values (which were considered to be constant):

$$0.05\text{–}0.08\text{–}0.12\text{–}0.14\text{–}0.18\text{–}0.25\text{–}0.50 \text{ min}^{-1}$$

In addition, many of the DTA curves were also simulated with our HP-65 programs with similar results.

Apart from the cell constant, four parameters must deal with the desired correction formulas,

(1) "temperature feedback" Θ_m (= max. temperature difference)
(2) activation energy E
(3) frequency factor k_∞
(4) heating rate m

Our computer programs render half width and shape index directly[15].

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*Simulation of a DTA curve with time-intervals of $\frac{1}{10}$ u, i.e., total ≈ 70 steps, is accomplished in 2–4 min.

Absence of temperature feedback. For very dilute solutions, the temperature difference recorded is so small that an exact linear increase of the sample temperature may be assumed. If h_c is the h-value for the finite cell constant c, but h_∞ the h-value resulting from eqn (20) ($c = \infty$), we obtain from our model calculations

$$h_\infty = h_c \cdot \frac{uc}{uc + \mathrm{f}(u)} \tag{25}$$

where f(u) is approximately given by

$$\mathrm{f}(u) = \frac{a_1}{u + a_2} \ (= \text{constant for low } u) \tag{26}$$

using $a_1 = 3.45$, $a_2 = 11$ (Table 3).

TABLE 3

TRANSFORMATION OF THE HALF WIDTH FOR $c \to \infty$

Test of eqns (25) and (26) and of f(u) (see text).

Reaction	u_m	f(u) *PDP 10*	f(u) *HP-65*	f(u) *eqn (26)*	*Deviation from average computer value (%)*
1	0.46	0.310±0.015[a]	0.303±0.015[a]	0.301	−2.0
2	0.88	0.281±0.023	0.272±0.021	0.290	−4.7
3	1.63	0.250±0.019	—	0.273	+9.0
4	2.28	0.268±0.072	0.250±0.027	0.260	−0.4
5	2.46	0.233±0.018	0.233±0.026	0.256	+9.8
6	3.888	0.212±0.035	0.207±0.043	0.232	+11.0
7	3.96	0.238±0.025	—	0.231	−2.9
8	4.45	0.189±0.025	0.228±0.015	0.223	+6.9
9	5.79	0.169±0.047	0.168±0.031	0.205	+22.0
10	5.78	0.185±0.017	0.178±0.037	0.206	+12.0
11	6.20	0.180±0.060	0.220±0.082	0.201	−4.2
12	8.05	0.136±0.035	0.173±0.038	0.181	+16.0
13	10.05	0.163±0.064	0.160±0.028	0.164	+1.5
14	11.08	0.120±0.035	0.214±0.025	0.156	−6.0
15	14.21	0.105±0.032	0.080±0.035	0.137	+49.2
16	15.09	0.071±0.058	0.157±0.026	0.132	+16.0
17	17.9	0.108±0.029	0.116±0.030	0.119	+6.3
18	17.93	0.160±0.045	0.164±0.045	0.119	−26.5
19	23.27	0.126±0.030	0.116±0.062	0.101	−16.5
20	33.33	0.115±0.050	0.106±0.051	0.078	−29.0

[a] Standard deviations.

Each value of f(u) is an average value of 5 to 6 simulations for different cell constants (range $0.05 < c < 0.50$; see text). In general, there is a slight increase or decrease with respect to c which is reflected by the standard deviations and could be considered by a more complicated formula.

This means that for low u values (low activation energy and/or high frequency factor) h_c is much higher than h_∞ and its correction is, therefore, strongly influenced by the cell constant; in the case of high u-values not. This is based on the fact that in the first case, the kinetic (chemical) information is restricted to the first, increasing part of the DTA curve, while the second (declining) part simply resembles a (physical) heat decay curve. However, in the extreme case of $u = 0$, we have only a vertical "reaction line" rendering no kinetic information. In contrast, for high u-values the kinetic reaction effect is rate-controlling and extended over the total curve, since the kinetic processes are slow compared with the thermal events.

Additional consideration of temperature feedback. If we perform an exothermic reaction, there will be an additional increase of the temperature which distorts the desired linearity of this quantity. Therefore, a correction to $\Theta_m \rightarrow 0$ seems helpful, since this would allow to discuss kinetic phenomena from the ideal rate curves.

Increasing temperature-feedback causes a more rapid increase of the reaction rate in the initial part of the curve so that the half width is reduced. The influence of Θ_m on the half width can be formulated by an empirical expression

$$h = \frac{h_c + a_3 \frac{m}{c} \Theta_m \ln 2}{1 + a_3 \Theta_m} \approx h_c(1 - a_3 \Theta_m) \tag{27}$$

which shows linearity for low Θ_m values, and where a_3 is constant for a particular reaction (cf. Fig. 1). The smallest h which could be observed for *high* Θ_m-values ($\Theta_m \rightarrow \infty$) corresponds to a spontaneous reaction, i.e. h is then determined by the heat decay process

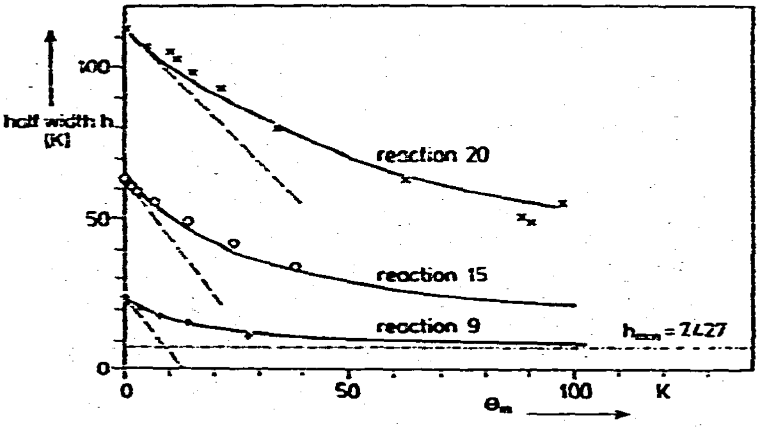


Fig. 1. Temperature feedback: Half width h and maximum temperature difference Θ_m for a particular cell constant ($c = 0.14$). Computer values (cf. Table 1): ×, reaction 20; $u = 33.33$. ○, reaction 15; $u = 14.21$. +, reaction 9; $u = 5.79$. Curves: h calculated from eqns (27) and (32). Inclined lines: Asymptotic straight line $h = f(\Theta_m/u)$ for low Θ_m values. Horinzontal line: half width for $\Theta_m \rightarrow \infty$.

$$\Theta = \Theta_0 e^{-c(t-t_0)} \tag{28}$$

using

$$h = T - T_0 = m(t - t_0) \tag{29}$$

and

$$\Theta = \tfrac{1}{2}\Theta_0 \tag{30}$$

Thus, the smallest h value is

$$h_{min} = \frac{m}{c}\ln 2 \tag{31}$$

The second limiting value, $h = h_c$ for $\Theta = 0$, is also reproduced by eqn (27). However, it seems astonishing that this simplest kind of a formulation for h also shows satisfactory agreements in the intermediate range. Considering other reactions also, our calculations showed that the value of a_3 may be formulated as a function of uc (and u),

$$a_3 = \frac{a_4 + a_5 \ln(uc)}{u} \approx \frac{a_4}{u} \tag{32}$$

where a_4 and a_5 are constants:

$a_4 = 0.36$ $\qquad$ $a_5 = 0.02$ $\qquad$ (cf. Fig. 1)

Insertion of a_3 into eqn (27) shows that Θ_m has to be referred to u,

$$h_x = \frac{h + \left(h - \frac{m}{c}\ln 2\right)(0.36 + 0.02\ln(uc))\cdot\frac{\Theta_m}{u}}{1 + \frac{3.45}{(u+11)uc}} \tag{33}$$

(*b*) *Shape index*

Absence of temperature feedback. For increasing cell constant c, a decrease of the shape index is to be expected since the second, decaying part of the curve is shortened. An adequate formulation which resembles that for the half width (eqn (25)) is

$$S_x = S_c \frac{(uc)^{b_1}}{(uc)^{b_1} + b_2} \tag{34}$$

when

S_c = shape index without temperature feedback

S_∞ = 0.55 (shape index for $c \to \infty$, see Section (3))

b_1 = 1.25 and $b_2 = 0.44$ are reasonable, unique values over the range $0.01 < uc < 10$ (Table 4).

Again, the deviations from the limiting value S_∞ are determined by the dimensionless product uc.

Additional consideration of temperature feedback. For an exothermic reaction, there is an increase of the shape index for increasing signal height Θ_m since the maximum of the curve is displaced to lower temperatures while the initial and the

TABLE 4

TRANSFORMATION OF THE SHAPE INDEX FOR $c \to \infty$

Test of eqn (34).

uc	$\dot{S}_d/S_\infty$[a]	$b_2 = (S_d/S_\infty - 1)\cdot(uc)^{b_1}$
0.02	42	0.308
0.04	21	0.358
0.06	14	0.386
0.1	8.3	0.410
0.2	4.5	0.468
0.5	2.15	0.484
0.6	1.90	0.475
0.8	1.60	0.454
1.0	1.45	0.450
1.2	1.38	0.477
1.4	1.30	0.457
1.6	1.20	0.360
2.0	1.13	0.309
3.0	1.08	0.315
5.0	1.07	0.523
10.0	1.06	(1.06)

[a] Extrapolated mean value from all u/c combinations tested which give a similar product uc. $S_\infty = 0.55$ (see text); $b_1 = 1.25$ (calculated from the HP-65 program STUD 14 A: Iterative solution of $f(x) = 0$).

TABLE 5

SHAPE INDEX AND TEMPERATURE FEEDBACK FOR A FIRST-ORDER DTA CURVE

Test of eqn (35) and (37).

uc Range	uc Representative value	$b_3 u$		No. of simulations
		From eqn (37)	From simulations and eqn (35)	
0.02–0.1	0.07	0.185	0.187 ± 0.065[a]	10
0.1–0.3	0.20	0.194	0.218 ± 0.074	22
0.3–1	0.65	0.225	0.223 ± 0.023	48
1–3	2.00	0.318	0.298 ± 0.028	40
3–10	5.50	0.560	0.545 ± 0.117	19

[a] Standard deviations.

final parts remain unchanged. At low feedback, S begins to increase from S_c linearly with respect to Θ_m (Table 5), but for higher signal heights a more exponential behaviour becomes evident, i.e., the two ranges are roughly covered by an expression

$$S = S_c(1 + b_3\Theta_m)e^{b_4\Theta_m} \approx S_c(1 + b_3\Theta_m) \qquad (35)$$

b_3 and b_4 are constants. b_4 may be positive or negative, the last term only being significant for high Θ_m values.

When Θ_m is increased for a certain reaction, the two points of inflection approach each other, and it becomes more and more difficult to determine the shape index accurately from a DTA curve. Simultaneously, the signal height (which for small Θ_m is proportional to the expression $[A]_0 V|\Delta H|/C_p$) shows a stronger increase until an unrealistic temperature difference is reached which, finally, in practice would cause an explosion-like evaporation of the solvent. Based on our simulations, the corresponding critical product is approximately given by

$$\left[\frac{[A]_0 V|\Delta H|}{C_p}\right]_{\text{crit}} \approx (13+0.8 \ln uc)\cdot u \tag{36}$$

Hence, for lower c-values the critical conditions are reached already at lower magnitudes of this product.

For the parameters b_3 and b_4, a dependency on uc and u similar to the correction formulas for the half width (eqns (27), (32) and (33)) was expected. As Table 5 illustrates, b_3 in eqn (35) indeed may be expressed in the following way:

$$b_3 = \frac{b_5 + b_6 uc}{u} \approx \frac{b_5}{u} \tag{37}$$

with $b_5 = 0.18$ and $b_6 = 0.069$.

For b_4, again the term ln (uc) is observed as in eqn (32),

$$b_4 \approx b_7 \ln (uc) \tag{38}$$

with $b_7 \approx -0.01$, although the accuracy of this value is not as high as for b_3 since only 2 to 5 simulations were performed for each reaction/cell constant combination in this range of high temperature differences ($\Theta_m \approx 0.5\,u$ up to $\approx 5\,u$). Such simulations are necessary for the detection of the deviations of S (Θ_m) from linearity (according to eqn (35)), but difficult. On the other hand, experimental conditions with so high temperature differences are undesirable for kinetic measurements because of the increasing temperature inhomogenities and approach to the explosion limit.

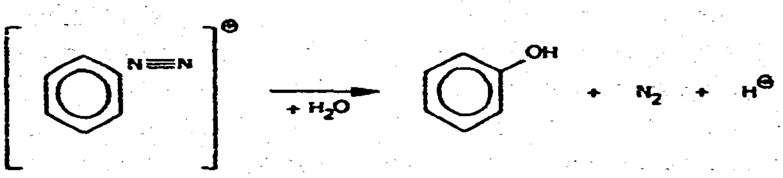
In conclusion, the ideal shape index S_∞ is obtained from the real one using the equation

$$S_\infty = \frac{(uc)^{1.25+0.01\,\Theta_m}}{[(uc)^{1.25}+0.44]\left[1+(0.18+0.069uc)\dfrac{\Theta_m}{u}\right]}\cdot S \tag{39}$$

This expression also shows the true limiting behaviour. S converges towards zero for infinitely high cell constant *and* signal height which we confirmed in the computer simulation of elementary rate curves.

DISCUSSION AND OUTLOOK

The correction formulas derived for the half width, h (eqn (33), and the shape index, S (eqn (39)), were checked by DTA experiments using a well-investigated system.



The decomposition of benzene diazonium sulfate occurs with liberation of nitrogen and is of first-order[6,18]. The DTA experiments were performed in our apparatus of a semi-calorimetric type primarily described in 1965[7]. After generation of the diazonium salt at ≈ 273 K in 1:5 dilute aq. H_2SO_4, the solutions were heated at a rate $m = 1.5$ K min^{-1}. Using five concentrations between 0.05 and 0.6 mol dm^{-3}, we found h and S data listed in Table 6.

TABLE 6

DECOMPOSITION OF BENZENE DIAZONIUM SULFATE: CALCULATION OF THE IDEAL HALF WIDTH AND SHAPE INDEX FROM EXPERIMENTAL DTA CURVES

$[A]_0$ (mol dm^{-3})	T_m (K)	θ_m (K)	h (K)	h_k (K)	S	S_k
0.05	335	0.84	22.8	18.75	0.90	0.55
0.05	332	0.97	21.0	17.34	0.85	0.52
0.1	336	1.93	21.3	18.32	0.93	0.55
0.1	334	2.08	21.6	18.70	0.91	0.53
0.2	336	3.27	21.6	19.62	1.08	0.60
0.2	337	4.05	22.3	20.92	1.11	0.60
0.4	338	8.56	19.8	21.47	1.22	0.57
0.6	341	13.38	18.0	22.04	1.55	0.64
0.6[a]	342	11.40	18.0	20.89	1.22	0.53

0.00 $c = \infty$ 331.5, $h_\infty = 19.15$, $S_\infty = 0.55$ (ideal value), h_k = corrected half width; S_k = corrected shape index. Data for correction: $c = 0.15$ min^{-1}; $u = 5.68$ min; $m = 1.5$ K min^{-1}.

[a] Twofold stirring rate.

In order to control the first-order type, the logarithm of the reaction rate constant (calculated from the equation of Borchardt and Daniels[6]) was plotted versus $1/T$ resulting in a straight line and an average activation energy of 27.5 kcal mol^{-1} and $\log k_\infty = 16.7$ (k_∞ in min^{-1}; lit.[1] $E = 27.2 \pm 1.5$ kcal mol^{-1}, $\log k_\infty = 16.8$). However, by digital computer simulation of the total curves based on *constant* cell constant c, differing values were obtained for the activation data: $E = 26.7$ and $\log k_\infty = 17.0$. From the latter and from eqn (14), the corresponding u value is seen to be $u = 5.68$.

Consequently, from eqn (20) and this u, $h_\infty = 19.15$ K is obtained if we assume a first-order process. As Table 6 demonstrates, the experimental h values, indeed, decrease, but the S values increase with enhanced temperature feed-back (sections 4a, 4b). Deviations of the corrected values from the ideal ones are expected from physical reasons. For low initial concentrations, an approach to the boiling point, for high concentration inhomogeneities in temperature may falsify the signal compared with theory. Therefore, at high concentration (0.6 m) and at a doublefold stirring rate (2 lifts per second instead of one only) a lower h and S value are obtained which show smaller differences to the theoretical ones (Table 6).

In Fig. 2, the experimental DTA curves for three concentrations 0.05, 0.2 and 0.6 mol dm^{-3}, referred to a unique signal height, are plotted. The influence of the feedback, reduction of half width as well as shape index are clearly represented. In comparison, a curve simulated by the pocket calculator HP-65 of Hewlett-Packard for very small feedback has been added. The deviations in the last part of the curve are due to the constant cell constant ($c = 0.15$) chosen and are avoided by using c as a temperature function[1].

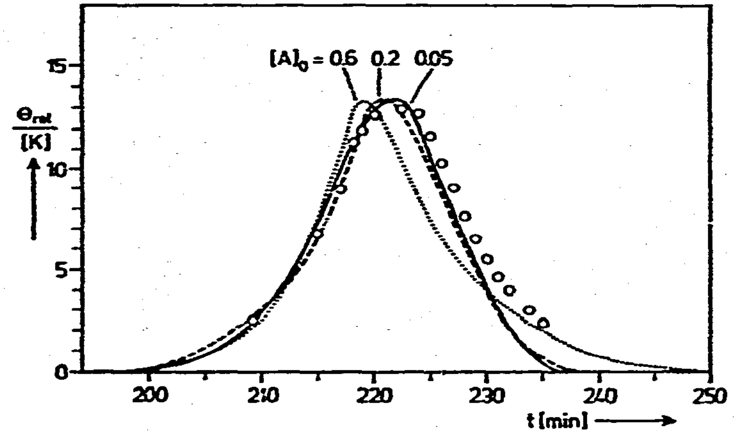


Fig. 2. DTA curves of benzene diazonium sulfate solutions for different initial reactant concentrations and neglegible temperature feedback (see text). $[A]_0$ mol/dm^{-3}. O——O, computer-simulated curve. Data: $\Delta t = \frac{1}{2}$ min^{-1}; $u = 5.34$ min; $c = 0.15$ min^{-1} = const. Hewlett Packard HP-65.

If we consider that, in reality, the c value increases with temperature, the approximate constancy of the corrected h and S values confirm the quantitative validity of the theory presented for a first-order process. This is additionally shown in Table 7 by data of some other reactions of this type which we investigated by DTA.

So, the correction formulas may be applied generally in the field of chemical reactions with detectable activation energies, since the numerical constants were tested over the total imaginable range of activation parameters. Of course, they may slightly be changed and optimized for special reaction parameter ranges occurring in a particular field of research by additional computer simulations, especially if the heating rate is very different from the optimum range for the study of reactions in solution, 0.2–4 K min^{-1}.

The expressions may be programmed in commercial pocket computers. Therefore, the correction of the "mechanistic indices" M and S to the ideal conditions may

TABLE 7

CALCULATION OF THE "MECHANISTIC INDICES" M AND S FOR SOME FIRST-ORDER REACTIONS STUDIED BY DTA (application of eqns (33), (39) and (20))

The u values were calculated from E and $\log k_\infty$ (determined by our analog computer program[1]) or from E (obtained from the equation of Borchardt and Daniels[6]) and T_m (cf. eqn (8)).

Subject	$[A]_0$ ($mol\,l^{-1}$)	m ($K\,min^{-1}$)	c (min^{-1})	Θ_m (K)	u (min)	h (K)	h_k (K)	M 10^3	S	S_k	*Ref.*
Decomposition of triphenyl phosphite ozonide (= I) in CH_2Cl_2	0.3	1.45	0.18	15.96	5.98	16.8	23.3	4.4	1.23	0.59	1, 5
	0.12	1.5	0.18	9.60	6.34	16.5	19.0	5.3	0.82	0.43	
Oxidation of 2,3-dimethyl butene-2 (excess) by I in CH_2Cl_2	0.037	1.17	0.15	2.35	7.94	35.0	33.9	3.5	0.84	0.58	3
Decomposition of *p*-ethoxy phenyl pentazole in methanol/water (7:1)	0.048	1.6	0.18	1.25	6.93	24.5	19.7	4.8	1.23	0.74	2
	0.036	1.75	0.18	0.18	4.69	17.8	14.2	5.9	0.75	0.48	
Decomposition of tris-(π-allyl) cobalt in ether	0.064	1.1	0.165	2.50	6.30	17.6	16.3	4.5	1.00	0.64	[a]
Decomposition of α-vinyl epidioxy dihydrofuran in tetrahydrofuran	0.11	1.16	0.15	0.65	5.00	18.5	14.6	4.1	0.88	0.55	8
Decomposition of di-isopropyl ether trioxide in di-isopropyl ether	0.656	1.13	0.185	6.90	5.02	15.8	14.8	4.0	1.13	0.57	5
Theoretical values for a first-order reaction (see text)	0.00	—	∞	0.00	—	—	—	4.7	—	0.55	

[a] We thank Dr. W. Pump for the preparation of the material; cf. W. Pump, *Doctoral Thesis*, University of Bochum, 1974.

be performed in a very short time. Hence, we have avoided to present the total evidence for all relationships presented; all facts are readily controllable in every laboratory.

All DTA relationships in Section (4) are empirical since things are too complicated for an accurate mathematical treatment. The striking feature of the expressions is that the product *uc* is similarly important for the description of the shape of a DTA curve of an elementary reaction as is the quantity *u* for the rate curve.

Without temperature feedback, the correction of S exclusively depends on *uc*: Taking half of the cell constant has the same influence as taking half of *u*, i.e., half of the activation energy (eqn (8)), the $\approx\sqrt{2}$-fold frequency factor or the doublefold heating rate. For correction of *h*, the situation is comparable, but there is a slight, additional influence of *u* itself (eqns (25) and (26)).

Involving temperature feedback, the signal height appears referred to *u* in both correction formulae which again confirms the important role of this quantity in non-isothermal reaction kinetics. The proposed formulae are surely valuable also for the diagnosis of unknown, complex reactions from their DTA curves, since *h* and S are readily available, and u_m may be calculated (after determination of E_0 in the initial range by the simplified equation proposed by Borchardt und Daniels[2,3,5,6]) from the maximum temperature T_m via expression (8). Then, the "ideal" mechanistic indices S and M_1 are available by the additional consideration of eqns (18) and (20).

We are continuing our work, especially with regards to complex reactions and the elementary second-order reactions which obviously show similar relationships, but with the inclusion of the initial concentration of the reactant.

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