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REACTION KINETICS AT LINEARLY INCREASED TEMPERATURE. IV. RELATIONSHIPS BETWEEN DTA CURVES, RATE CURVES AND ADIABATIC CALORIMETRY

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ABSTRACT

A general concept is presented for the kinetic interpretation of DTA curves. This is based on the limiting conditions of a DTA measurement: either the kinetic cell constant is zero (adiabatic conditions), or infinite (rate curve). On the other hand, the self-heating effect (thermal feedback), based on the product of the reaction enthalpy with the reactant feed, may be absent ("ideal" kinetic DTA curve) or infinite (impulse reaction). Our recent formulae for the correction of the kinetic classification parameters, shape index and reaction type index, as well as other relationships and their utility, are successfully tested by application to ca. 2000 experimental DTA curves obtained in stirred solutions.

The expressions reveal the influence of the activation parameters, heating rate, maximum signal height and cell constant and, therefore, allow a general discussion of the kinetics, independent of the experimental conditions.

INTRODUCTION

A phenomenon typical of DTA curves is that the desired linear change of the sample temperature with time is falsified by the heat effect of the chemical reaction. Though the resulting temperature deviation—when measured as difference of the sample temperature versus reference temperature—is the source of the DTA method, it causes considerable difficulties for the absolute kinetic interpretation which should also usually correspond to the ideal condition of constant temperature increase in the sample [1–4].

With a view to reactions in solution performed in an "all-liquid" apparatus, empirical relationships have been developed which allow reference of the kinetic classification parameters, shape index and reaction type index, to the ideal kinetic conditions [5–7]. Because of the complex mathematics, it is not possible to derive analytical expressions from mathematical sources, as for the Arrhenius equation, the rate law, the heat balance equation (Newton's law) and proportionality between reaction rate and the generated heat flow. However, computer modelling has revealed that many relationships in DTA

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kinetics are approximately based on the product of specific time, u, and kinetic cell constant, c (uc-theory), apart from other terms based on u exclusively. This reveals a theoretical access to the understanding of the present expressions.

In this publication, the validity and the consequences of the uc-theory are discussed, on the basis of nearly 2000 exothermic DTA curves obtained in an all-liquid apparatus. As a source for the correction formulae, the limiting cases of a DTA measurement are considered, which represent the temporal measuring curves in the fields of adiabatic calorimetry, heat dissipation, thermal autocatalysis and usual rate-based chemical kinetics. Although the uc-theory is only a rough approximation, it opens up a way to better planning and evaluation of DTA experiments with a view to the variation of experimental conditions, such as concentration of reactants, heating rate, solvent, cell constant, temperature range, etc.

GENERAL uc-THEORY FOR AN ALL-LIQUID SYSTEM

Assuming uniform temperature in a solution, thermal symmetry of sample and reference sample, the absence of considerable self-heating, the validity of the Arrhenius and Newton equations [2,5,8,9], and use of a temperature-independent cell constant, the DTA curve for a first-order reaction is given by

$$\theta(t)=\frac{V|\Delta H|}{C_\mathrm{p}}[A]_0\Big\{\exp[-c(t-t_0)]-\exp(-uk)$$

$$+c\exp[-c(t-t_0)]\int_0^t\exp[c(\xi-t_0)-uk]\mathrm{d}\xi\Big\} \tag{1}$$

where $\theta(t)$ = temperature difference sample/reference with time; V = volume of sample; ΔH = reaction enthalpy; C_p = heat capacity; $[A]_0$ = initial concentration of reactant; c = kinetic cell constant; $k(t)$ = rate constant; $uk = {}_0^t\!\int k(\xi)\mathrm{d}\xi$.

The parameter u [5] may be approximately taken as constant with time and identified with u at the signal maximum

$$u_\mathrm{m}=\frac{E}{mR(\ln k_\infty+\ln u_\mathrm{m})^2}=\text{const.} \tag{2}$$

where E = activation energy; k_∞ = pre-exponential factor; R = gas constant; m = heating rate. The fundamental role of this "specific time" for non-isothermal reaction kinetics had been presumed from the theory of adiabatic explosion [10,11] and was confirmed by numerous experiments and computer simulations resulting in the definition of the reaction-type index [8,12,13].

Although an exact and explicit algebraic expression for $\theta(t)$ cannot be derived from eqn. (1), rough approximation functions for this value and other important quantities could only be found using tedious procedures [2]. Such relationships contain the typical term *uc*, suggesting an important role of this dimensionless product in the theory of DTA kinetics.

As an example for the significance of this product, the maximum temperature difference, θ_m, may be considered for a first-order process. An approximate expression had been predicted [2]

$$\theta_m = F\left(\frac{a}{(uc)^n}\right) - d \tag{3}$$

where a, d and n are empirical parameters. The calorific factor F is given by

$$F = \frac{|\Delta H| V [A]_0}{C_p} \tag{3a}$$

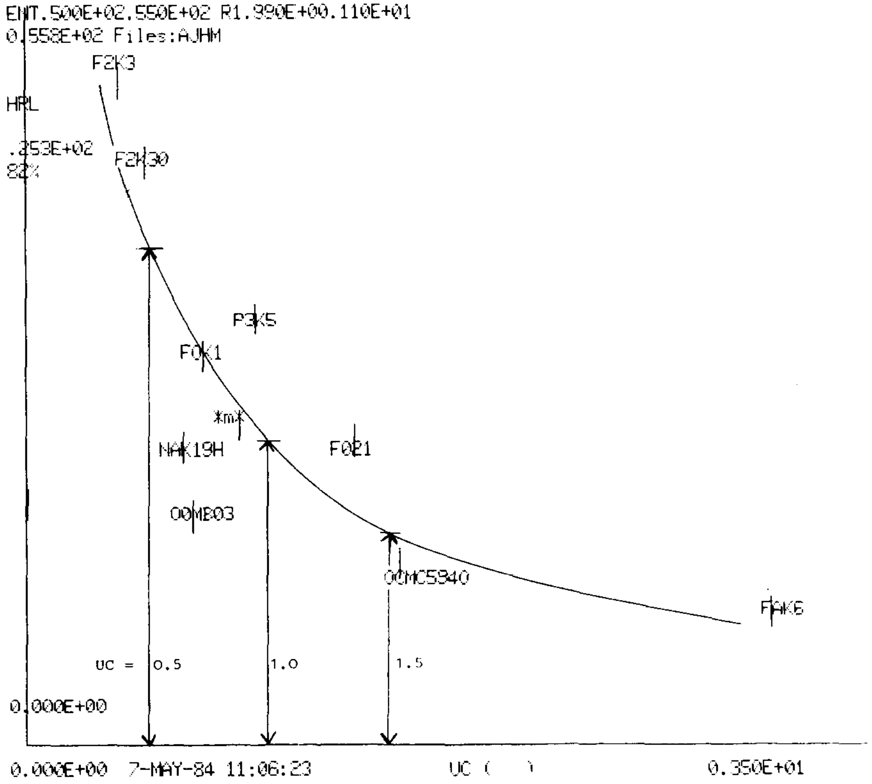

Fig. 1. Computer printout, used for the calculation of b and n in eqn. (6). Abscissa, product *uc*; ordinate, relative signal height $\theta_m/[A]_0$; $-\Delta H = 52.5 \pm 2.5$ kcal mol^{-1}; $r > 0.99$. The file names are also presented; $* m *$ means an average value of the ordinate, here obtained from two experiments.

TABLE 1

Determination of parameters n and b in eqn. (6)

$-\Delta H$ (kJ mol)			Number of experiments [a]					$\theta_m/\|A\|_0$ ($uc=1$)	b	n from $\theta_m/(uc)^n$ for $uc=$		Average n
Min.	Average	Max.	SUB	KOBIB	OLD	OZ	Total			0.5	1.5	
1	1.4	1.7	3	0	2	1	6		–			
1.9	2.1	2.3	2	0	0	4	6		–	0.85	1.38	1.12
3.8	4.2	4.6	1	0	0	5	6	0.3	0.071			
9.2	9.6	10.0	1	0	0	1	2					
20.9	23.0	25.1	2	0	4	0	6	3.42	0.148	0.51	1.15	0.82
25.1	28.3	31.4	1	0	5	2	8	3.4	0.120			
31.4	34.6	37.7	2	0	6	3	11	3.8	0.109	–	0.87	0.87
37.7	41.8	46.0	2	0	11	3	16	4.8	0.114	0.99	1.30	1.14
46.0	50.2	54.4	0	0	9	0	9	2.3	0.045	0.75	1.38	1.07
54.4	58.6	62.7	2	0	5	3	10	2.0	0.088			
62.7	69.0	75.3	2	1	9	1	13	12.62	0.181	0.78	1.26	1.02
75.3	83.7	92.0	0	1	12	2	15	7.3	0.087	1.05	1.19	1.12
92.0	98.3	104.6	2	2	1	2	7	7.3	0.074	0.43	1.48	0.95
104.6	113.0	121.3	0	0	8	3	11	12.4	0.114	0.33	0.54	0.43

121.2	127.5	133.8	0	0	9	5	14	12.5	0.097	0.75	0.55	0.65
133.8	142.2	150.6	1	1	4	5	11	11.4	0.080			
150.6	159.0	167.4	1	0	12	2	15	18.0	0.113			
167.4	177.8	188.2	0	1	12	4	17	21.1	0.118			
188.2	198.7	209.2	0	1	17	3	21	21.9	0.110			
204.2	219.7	230.1	3	1	10	6	20	25.8	0.117	0.64	0.87	0.76
230.1	242.7	255.2	1	0	19	7	27	28.1	0.115			
255.2	269.9	284.5	0	3	19	9	31	35.1	0.129			
288.6	301.2	313.8	0	2	10	7	19	29.8	0.099			
313.8	328.5	343.1	1	1	14	6	22	36.2	0.110	0.36	0.70	0.53
343.1	359.9	376.6	0	0	12	4	16	37.5	0.104			
376.6	397.3	418.4	0	3	13	4	20	41.3	0.104	0.68	0.79	0.73
418.4	439.3	460.2	2	1	7	1	11	36.0	0.082			
460.2	483.3	506.3	2	1	6	2	11	43.1	0.088	0.46	0.47	0.47
502.1	523.0	543.9	3	2	2	8	15	25.2	0.048			
543.9	564.8	585.7	4	2	4	0	10	25.2	0.044			
585.7	617.1	648.5	1	1	5	1	8	31.6	0.051		0.50	
648.5	700.8	753.1	2	2	3	2	9	35.4	0.050		0.77	

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[a] SUB = subsystems of oscillating systems; KOBIB = autocatalytic systems, e.g., $NaIO_3 + H_2O_2$; OLD = various systems (oxidations, triphenylphosphite reactions, Diels–Alder, decomposition of peroxides, etc.); OZ = oscillating systems.

On the basis of numerous theoretical DTA curves, the following values were found: $a = 0.52$, $n = 0.6$ and $d = 0.23$. Re-investigating ca. 2000 exothermic experimental DTA curves stored in our computer library, eqn. (3) has been studied in greater detail in order to calculate the coefficients a, n and d more accurately. About 500 sets of DTA curves of obvious first-order reactions, with correlation coefficients for the Arrhenius plots of > 0.99, were picked up and classified with respect to the enthalpies yielding 33 groups with similar enthalpies ($\Delta\Delta H \approx \pm 8\%$), and covering the range from $\Delta H = -2.09$ to -753 kJ mol^{-1}. The graphs of the relationships

$$\theta_m/[A]_0 = f(uc) \tag{4}$$

obtained by our library searching program [3,14], were printed out for all of the series (e.g., Fig. 1). A first evaluation of these plots was based on the assumption that $uc = 1$ and dividing the values for $\theta_m/[A]_0$ by the enthalpy giving a nearly constant factor, b, up to heats of 420 kJ mol^{-1} for the respective group (Table 1, Figs. 1 and 2)

$$b = \frac{f(uc)}{|\Delta H|} = \frac{aV}{C_p} \tag{5}$$

The term d of eqn. (3) is neglected. It is remarkable that b is not decreased for reaction heats lower than 420 kJ mol^{-1}, although numerous experiments with strong self-heating (signal height, θ_m, from 0.05 to 20 K!) were included in our test.

Subsequently, the additional use of $f(uc)$ for the uc values 0.5 and 1.5 enable the n exponent in eqn. (3) to be calculated (Table 1, Figs. 1 and 3). This kind of procedure leads to a stepwise increase of n for $|\Delta H| < 85$ kJ mol^{-1} and to a divergence up to $\Delta n = \pm 0.38$ between n values for low and high uc (Fig. 3). Hence, under the conditions $C_p = 18.8$ J K^{-1} and $V = 5$ ml, eqn. (3) is simplified to

$$\theta_m \approx F\frac{a}{(uc)^n} = \frac{b|\Delta H|[A]_0}{(uc)^n} \approx 0.11|\Delta H|[A]_0\left[\frac{mR(\ln k_\infty + 2.5)}{Ec}\right]^n \tag{6}$$

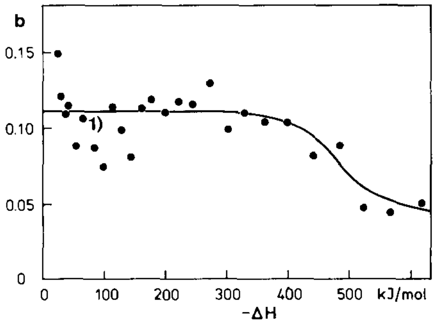

Fig. 2. Is the factor b in eqn. (6) independent of the reaction enthalpy? (1) Average of two groups (50.2 and 69.0 kJ mol^{-1}); (———) assumed dependence (see text).

using

$$n \approx 0.65 + 57\left(\frac{3.5 + uc}{73.2 + |\Delta H|}\right)^2 \tag{6a}$$

The second term in eqn. (6a) may be neglected for high enthalpies; it considers the deviation of n from constancy, which is striking for high uc terms, and partially caused by the neglection of the d term in eqn. (3) and variations of the C_p values of the solvent. Roughly, the n-values may be chosen from the following list.

$-\Delta H$	4–80	> 125 kJ mol^{-1}
$0.1 < uc < 0.8$	0.87	0.65
$1.2 < uc < 10$	1.15	0.68

The factor b must be calibrated for a certain apparatus. Hence, eqn. (6) is a practicable tool for the prediction of the absolute peak height of a first-order reaction to be studied when the cell constant, heat capacity, heating rate, enthalpy, reactant feed $[A]_0$ and activation data E and k_∞ are approximately known.

The preferred application of the uc-theory is for the estimation of special data of the ideal kinetic rate curves, based on the absence of heat feedback ($\theta_m = 0$) and infinite cell constant, c, from any experimental DTA curves [5–7].

LIMITING CASES OF REAL DTA CURVES

Figure 4 shows, in the centre, a typical DTA curve of a first-order reaction. This curve is surrounded by eight other curves which can be derived from linear temperature increase of the heating bath; these represent

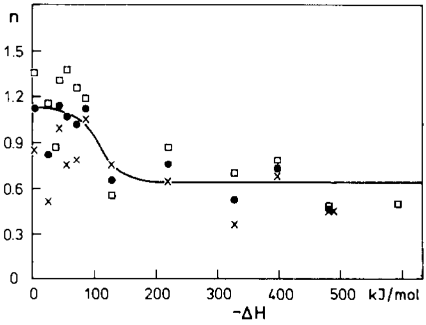

Fig. 3. Exponent n in eqn. (6), plotted vs. the reaction enthalpy: (×) n for $uc = 0.5$; (□) n for $uc = 1.5$; (●) mean of both n values; (———) eqn. (6a).

limiting cases of the DTA technique with respect to the cell constant, c, and the maximum temperature difference, θ_m. Apart from the actual value, the arrangement of the curves is based on the assumption of two limiting values for both parameters: zero and infinity. Six cases are of major importance:

(1) ideal adiabatic curve with $\theta_m \rightarrow 0$ (hypothetical case!);
(2) heat impulse curve (step function);
(3) ideal DTA curve (no heat feedback);
(4) heat–decay curve;
(5) ideal rate curve (approximately monitored by techniques using rate-proportional measuring quantities, such as DTG, derivative EGA, heat-compensating DSC, following of optical extinction, especially in an all-liquid apparatus) [15];
(6) rate impulse curve (vertical straight line!).

For the validity of eqn. (6), θ_m has to show a similar inverse correlation to both the specific time, u, and the cell constant, c. Consequently, an increase in the heat feedback effect, obtainable by choosing a higher starting concentration of reactant, causes the same modification of the DTA curve as a deceleration of the u-value, obtainable by selecting a reaction with lower activation energy or higher frequency factor, or taking a higher heating rate; cf. eqn. (2). The curve then becomes higher, but smaller, and the time range which yields information on chemical kinetics is reduced, whereas the time range which allows information on heat-decay kinetics to be obtained, is

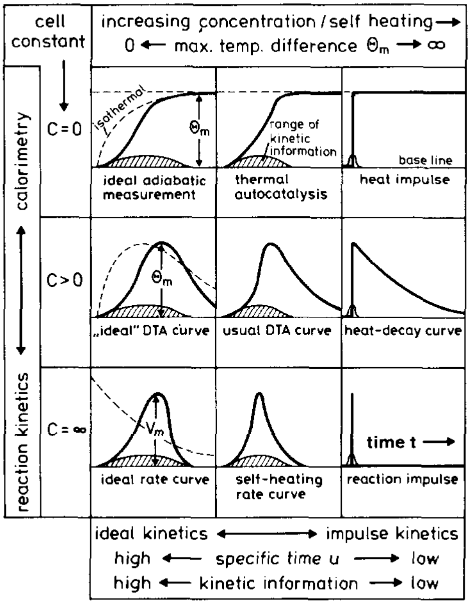

Fig. 4. The limiting cases of all-liquid DTA curves. A first-order reaction was assumed; the shaded areas visualize the extent of kinetic information to be obtained for a definite time.

extended. A decreasing cell constant has the same influence upon the signal height, but not on the signal form because there is no u/c-changeability in eqn. (1) [9].

The impulse functions (cases 2 and 6) illustrate that even a characteristic temperature, such as the step temperature, gives information on chemical kinetics, but restricted to a superposition of both activation parameters contained in the specific time u (eqn. 2). According to the Arrhenius equation, the initial temperature for leaving the noise level, χ, of a rate curve is represented by [3,13,15,16]

$$T_0 = \frac{E}{R(\ln k_\infty + \ln u - \ln \chi)} \approx \frac{E}{R \ln k_\infty} \tag{7}$$

A similar equation, involving the cell constant, is valid for a DTA curve [2,12,16–18]. Usually, $\ln u - \ln \chi \ll \ln k_\infty$, and heat feedback can be excluded at the noise level. Therefore, the ratio $E/\ln k_\infty$ may be approximately calculated from T_0. Because of the disappearing time interval (and the disappearing temperature interval), E and $\ln k_\infty$ cannot be obtained separately from these impulse functions. Hence, relationships such as eqn. (7) may be seen as one reason for the well-known kinetic compensation effect [19–22] when experiments performed at similar temperatures are compared.

The special potential of the uc-theory lies in the possibility of scaling the kinetic information content of any DTA or other non-isothermal reaction curve by the use of easily accessible and managable data, such as θ_m, u, c and m (cf. Fig. 4).

Further, a discussion of the limiting cases is essential for obtaining an idea of the reaction scheme, independent of the parameters of the apparatus. Assuming 20 definite first-order reactions and calculating theoretical DTA plots by the use of special integration programs [5,7,23,24], we could show that the halfwidth, h, and shape index, S, can be obtained from the ideal quantities using the empirical expressions for $c = \mathrm{const}$,

$$h_\mathrm{exp} = \frac{h_\infty\{1 + a_1/[(a_2 + u)uc]\} + a_4 h_{\infty c}\theta_\mathrm{m}/u}{1 + a_4\theta_\mathrm{m}/u} \tag{8}$$

$$S_\mathrm{exp} = S_\mathrm{ideal}\frac{\left[(uc)^b + b_2\right]\left[1 + (b_5 + b_6\, uc)\theta_\mathrm{m}/u\right]}{(uc)^{b_1 + b_4\theta_\mathrm{m}}} \tag{9}$$

with the following empirical constants [5]:

a_1, a_2 = adaption parameters for absence of feedback (also useful for the estimation of product uk at the DTA peak [2]);
a_1 = 3.45; dominates in the adiabatic case ($c \to 0$);
a_2 = 11; dominates in the reaction-impulse case ($u \to 0$);
a_4 = $0.36 + 0.02 \ln(uc) \approx 0.36$; calibration parameter for the feedback effect;

TABLE 2

Consequences of the *uc*-theory for haldwidth and maximum height of a first-order signal

Case	Heat decay conditions and effects on infinite thermal feedback (→)	Halfwidth		Maximum height [a]	
		$\theta_m \to 0$	$\theta_m \to \infty$	$\theta_m \to 0$	$\theta_m \to \infty$
1 2	$c = 0$ adiabatic calorimeter → heat impulse	∞	∞	$\left(0.44 F \frac{a_2 + u}{a_1}\right)$ [b]	F
	$c \ll u$ DTA; heat conduction dominates	$2.25 mu \left[1 + \frac{a_1}{(u + a_2) uc}\right]$	$\frac{2.25 mu + a_4 \ln 2 (m/c)(\theta_m/u)}{1 + a_4(\theta_m/u)}$	$0.44 F \frac{a_2 + u}{a_1}$	Very complicated [c]
3 4	$c \approx u$ usual DTA curve → heat decay curve	eqn. (8) [a]	$\frac{m}{c} \ln 2$	$0.44 \frac{F}{(uc)^{0.6}}$ [a]	$\frac{F}{\ln 2}$
	$c \gg u$ DTA; reaction kinetics dominate	$2.25 mu (1 + \frac{a_1}{a_2 uc})$	$\frac{m}{c} \ln 2$	$0.44 \frac{F}{uc + (a_1/a_2)}$	$\frac{F - 2.25(u/a_4)(uc + (a_1/a_2))}{\ln 2}$
5 6	$c \to \infty$ reaction rate curve → reaction impulse	$2.25 mu$	$\frac{2.25 mu^2}{a_4 \theta_m} + \frac{m}{c} \ln 2 \to 0$	$0.44 \frac{F}{uc} \to 0$	$\frac{F}{\ln 2 + 2.25(u^2 c / a_4 \theta_m)}$

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[a] See text.

[b] Since the correct value is F, this expression is only valid for one (unrealistic) u value.

[c] $\theta_m = \frac{F}{2 \ln 2} - \frac{2.25}{2} \frac{u^2 c}{\ln 2} + \sqrt{\left(\frac{F}{2 \ln 2} - \frac{2.25}{a_4 \ln 2}\right)^2 + \frac{u}{a_4 \ln 2}} - F.$

b_1 = 1.25; describes the influence of the reaction order; $b_1 = 2$ for second order;
b_2 = 44; defines the contribution due to the adiabatic case;
b_4 = 0.01; calibration parameter, remarkable only for strong feedback;
b_5 = 0.18; $b_6 = 0.069$; causes a linear increase in S_{exp} with respect to θ_{m} for small or medium feedback effects (analogous to a_4).

Further, we have the fundamental constituents

$$h_{\infty} = 2.25mu \text{ (ideal rate curve)} \tag{9a}$$

$$h_{\infty c} = (\ln 2)\, m/c \text{ (heat decay curve)} \tag{9b}$$

The formulations (8) and (9) were constructed in such a manner as to include the important limiting cases in Fig. 4. As a consequence, the necessarily empirical correction expressions show inaccuracies in certain ranges of the parameters, especially for high u or low A factors (which, fortunately, corresponds to small corrections), and for strong heat feedback. This disadvantage may be circumvented by special optimization of the empirical constants a_i and b_i in the ranges which are usual in a laboratory.

As Table 2 shows, eqn. (8) leads, indeed, to the expected quantitative expressions for h in cases 3, 4 and 5, to the required zero value of h in case 6 and to an infinite h value in cases 1 and 2. The equation is, and also eqn. (9), plausibly based on the terms uc (stemming from the Newton law using first-order heat decay) and θ_{m}/u (obtained from the theory of adiabatic explosion).

Moreover, Table 2 presents the approximate expressions for the maximum temperature difference, θ_{m}, partially deduced from the very rough assumption that the area under a DTA curve is equal to the rectangle $h \times \theta_{\mathrm{m}}$. This yields the equation (cf. refs. 5, 25)

$$\theta_{\mathrm{m}} = \frac{mF}{ch} \tag{10}$$

Relationships similar to eqns. (8) and (9) were deduced for the second-order processes $A + A \rightarrow$ products and $A + B \rightarrow$ products [6,7].

DISCUSSION

Since their development, relationships (8) and (9) and the analogous relationships for second-order kinetics were frequently used for the interpretation of DTA experiments in our laboratory, especially in concentration or heating-rate series. Hence, their applicability seems confirmed because numerous convergence points were discovered in the mechanistic S/M diagrams for more than 100 reacting systems, signalling rate-determining steps in the corresponding mechanisms [3,13,14,26].

For a powerful verification of eqns. (8) and (9), all of our existing first-order DTA curves were selected using our computer-library search program. As conditions, the following parameter ranges were fixed: the first-order correlation coefficient for validity of the Arrhenius equation, $r_1 > 0.99$; the heating rate, $1.2 < m < 1.8$; and discrete ranges of the signal height, (1) $0.2 < \theta_m < 0.5$ K (weak feedback), (2) $0.5 < \theta_m < 7$ K (medium feedback), (3) $7 < \theta_m < 12$ K (strong feedback), and (4) $12 < \theta_m < 25$ K (extreme feedback). The reaction-type indices in the preferred range of medium feedback are presented in Fig. 5, as a function of the peak height. There is a statistical scatter around $\overline{M}_1$ corresponding to first order (0.020 kJ mol^{-1} K^{-1}), indicating that: first, we really have an approximate first-order reaction; second, that there is no systematic influence of θ_m upon M, i.e., the feedback term in eqn. (8) is really justified (Table 3). The deviations could be caused by the very different activation data of the various systems investigated [3,14,27,28], but also because the correlation coefficients are not at all necessarily characteristic of a first-order reaction: special mechanisms exist,

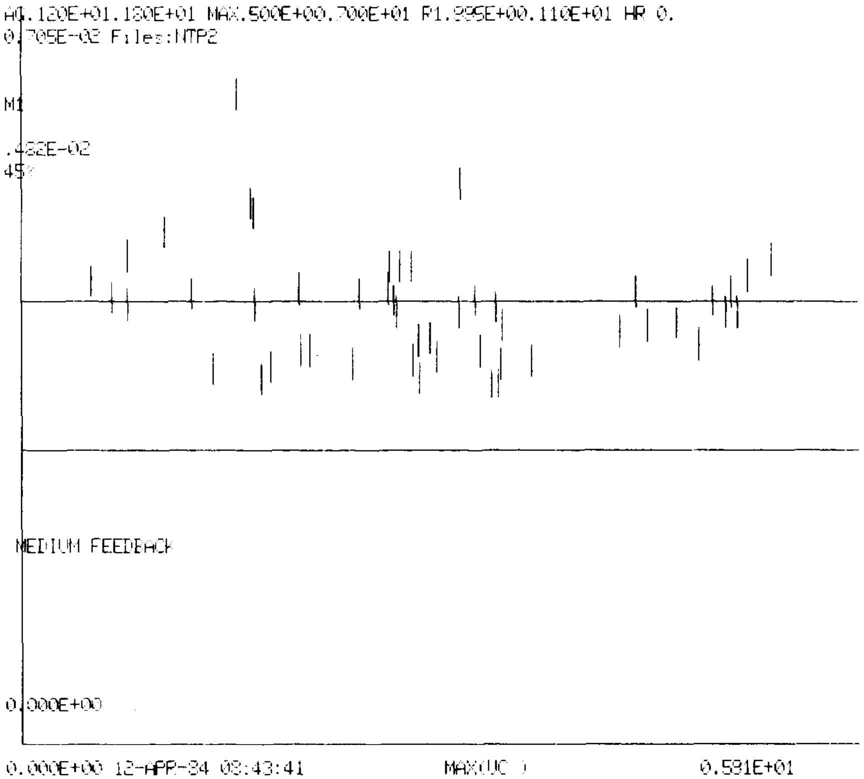

Fig. 5. Approach to the ideal M value (= 0.00199 kJ mol^{-1} K^{-1}) for 52 experiments involving medium heat feedback. Abscissa, maximum signal height; ordinate, M value, referred to a first-order gross reaction. Lower and upper horizontal line, $M = \overline{M}_2$ and $M = \overline{M}_1$, respectively, m = 1.2–1.8 K min^{-1}; $r > 0.995$.

TABLE 3

Test of the *uc*-theory: the mechanistic indices of first-order DTA experiments

Conditions	No. of expts.	M value		S value	
		average ($\text{kJ/mol}^{-1}\ \text{K}^{-1}$)	standard deviation (%)	average	standard deviation (%)
$0.1 < uc < 0.3$	12	0.0215	9.7	0.73	19
$0.3 < uc < 2$	45	0.0189	13	0.59	15
$2 < uc$	30	0.0207	4.5	0.62	9.5
$0.2 < \theta_m < 0.5$	21	0.0207	8.8	0.65	22.8
$0.5 < \theta_m < 7$	56	0.0187	6.7	0.65	15.6
$7 < \theta_m < 12$	7	0.0223	20.2	0.67	7.1
$12 < \theta_m < 25$	3	0.0217	2.8	0.51	24.5
Total/average	87	0.0199	9.6	0.62	13.7
theory	—	0.0199		0.58	

e.g., $A + B \rightarrow 2B$, which assume a first-order straight line in the Arrhenius diagram.

The resulting corrected S values are generally ca. 7% higher than $S_1 = 0.58$ (Table 3), because the determination of the maximum slope in the increasing part of an experimental signal is severely handicapped by fluctuations of the second derivative. Therefore, a straight-line fit in a time interval with the first inflection point in the centre was used.

If the influence of the product *uc* on M and S, is taken into account it becomes obvious that there is a satisfactory validity of eqns. (8) and (9) in the range $0.3 < uc < 2$, whilst for lower *uc* values, M and S are increasingly higher than $\overline{M}_1$ and S_1. For $uc > 2$, only the M values show smaller positive deviations from the reference value.

In cases of strong or extreme feedback, the results with eqn. (8) are quite satisfactory, whereas the corrected shape index (eqn. 9) reveals rather distinct deviations from S_1. However, with strengthened feedback, the shape-index determination of the increasingly needle-like DTA curves (Fig. 4) becomes increasingly difficult. Then, the scatter is predominantly statistical, but reveals no systematic deviations which would indicate that eqn. (9) is invalid.

In the case of the kinetically ideal conditions of small feedback, the mean values of M and S are approximately equal to $\overline{M}_1$ and S_1, but there is a much stronger scatter of the shape index and of the M index if the latter is referred to the initial, not to the gross, activation data. This reflects an approach to the noise level of the DTA equipment. The product $[A]_0|\Delta H|$ which is essential for the temperature effect θ_m, becomes too low for satisfactory measuring conditions. Table 4 gives various examples of experiments and the condition parameters as well as the resulting mechanistic indices.

TABLE 4

Examples of DTA plots revealing nearly first-order behaviour ($r_1 > 0.99$)

Molarities/components/solvent	θ_m (K)	m (K min^{-1})	u_m (min)	uc	h		S		M_1 [a] (kJ mol^{-1} K^{-1})
					exp. (K)	corr. (K)	exp.	corr.	
Weak feedback									
0.05 benzene adduct [b] +0.5 isoprene/pentane [c]	0.11	0.86	5.39	0.91	12.9	10.6	1.03	0.64	0.0198
0.45 BMA/1.5 M aq. H_2SO_4	0.12	2.22	3.01	0.32	31.1	14.8	1.48	0.56	0.0206
0.086 indene ... O_2 [b]/THF [c]	0.29	1.45	10.91	3.12	36.4	34.1	0.57	0.54	0.0211
0.0075 $KMnO_4$ +0.75 MA/H_2O	0.37	1.54	2.15	0.24	16.1	8.0	2.4	0.68	0.0189
0.12 PhSOPh (Ar-gas)/$PhCH_2Ph$	0.39	1.66	6.25	2.23	29.9	26.4	0.79	0.67	0.0170
0.013 FFA...O_2 [b] +0.76 PPh_3/THF	0.49	1.00	9.86	2.39	23.2	22.1	0.72	0.63	0.0207
0.21 tr-CON + 1.25 CHD/cyclohexane [c]	0.66	1.56	6.81	1.21	27.1	23.0	0.84	0.63	0.0193
0.055 PO_3 + 1 CHD/CH_2Cl_2	0.78	0.29	42.8	5.95	23.7	23.6	0.61	0.58	0.0210
2 O_3(abs) [d]/DIPE [c]	0.79	0.54	9.25	1.64	14.8	14.1	0.70	0.59	0.0204
Medium feedback									
0.2 aniline [e] +0.05 $NaNO_2$/aq. H_2SO_4	0.84	1.55	5.11	0.72	22.6	18.0	1.02	0.58	0.0200
0.068 $NaBrO_3$ + 2.5×10^{-4} $MnSO_4$ [f]/1.25 M aq. H_2SO_4	0.93	1.39	7.33	0.73	30.3	22.0	0.78	0.44	0.0210
0.1 $NaBrO_3$ +0.525 NaBr +0.25 $Ce(SO_4)_2$ [f]/1.25 M aq. H_2SO_4	1.13	0.74	13.47	21.72	23.3	23.6	0.62	0.59	0.0209
0.25 $(OPh)_3PO_3$ +0.8 TME/CH_2Cl_2 [c]	1.16	1.97	5.30	0.99	20.4	24.3	1.16	0.63	0.0194
0.1 O_3(abs) [d]/DIPE	1.72	1.33	4.80	0.67	18.0	14.7	0.99	0.65	0.0197
0.08 $NaIO_3$ +0.528 H_2O_2/H_2O [c]	1.73	0.41	14.89	2.21	13.9	13.6	0.66	0.51	0.0204
0.025 $NaIO_3$ +0.528 H_2O_2/H_2O [c]	2.08	0.78	8.08	1.41	14.5	13.9	0.73	0.54	0.0205

0.08 2,4-DMF...O_2 +0.34 PPh_3/THF [c]	2.22	1.57	6.49	1.64	23.7	[illegible]	[illegible]	[illegible]	[illegible]
0.1 aniline [e] +0.2 $NaNO_2$/aq. H_2SO_4	3.33	3.13	2.43	0.37	25.9	18.4	1.70	0.57	0.0204
0.34 furan...02/CH_3OH	3.49	1.31	4.82	0.66	16.8	14.7	0.93	0.54	0.0195
0.3 *p*-toluidine [e]/aq. H_2SO_4	3.55	1.36	4.87	0.80	17.3	16.9	0.75	0.52	0.0178
0.055 $(OPh)_3PO_3$ +1 CHD/CH_2Cl_2 [c]	3.74	3.03	3.36	0.63	29.1	26.3	1.08	0.53	0.0192
0.055 $(OPh)_3PO_3$	4.40	1.59	4.40	0.80	19.3	17.8	0.96	0.66	0.0171
0.17 furan...O_2 [b]/CH_2OH [c]	4.82	1.62	6.12	1.00	23.5	23.8	0.99	0.59	0.0189
0.3 *o*-toluidine [e]	4.99	1.36	3.93	0.49	16.2	14.3	1.33	0.68	0.0169
Strong feedback									
0.22 furan...O_2 [b]/CH_3OH [c]	9.10	1.45	6.56	1.09	19.8	25.7	1.18	0.63	0.0192
0.055 $(OPh_3)_3PO_3$ +0.3 $(OPh)_3P$/CH_2Cl_2 [g]	9.51	1.50	8.28	1.23	24.5	28.4	1.24	0.74	0.0198
1.34 O_2(abs) [d]/DIPE	11.8	1.30	5.51	1.03	12.0	16.9	1.46	0.73	0.0191
0.08 $NaIO_3$ +0.587 H_2O_2 +0.001 $MnSO_4$/1 M aq. H_2SO_4	11.9	1.52	7.58	0.79	19.9	19.2	1.29	0.62	0.0194
							Theory:	0.58	0.0199

Abbreviations: DIPE = diisopropylether; THF = tetrahydrofuran; CHD = 1,3-cyclohexadiene; MA = malonic acid; BMA = monobromomalonic acid; DMF = 2,5-dimethylfuran; FFA = furfurylamine; CON = tr-cyclooctenone-(2); TME = 2-methylbutene-(2).

[a] $M_1 = R(\ln 10)^2 \, mu_m/h$, cf. ref. 5.

[b] Generated by photosynthesis.

[c] Pseudounimolecular.

[d] Calculated from the O_3 contribution in the oxygen stream.

[e] After diazotation at 0 °C.

[f] Presence of 0.375 MA.

[g] Bimolecular.

CONCLUSION

Summarizing both the recent results of the computer simulations and the novel studies of the approximate expressions cited and tested by the total number of DTA curves studied, leads to an optimistic view: experiments in an all-liquid apparatus [25] allow an absolute kinetic interpretation even under very different measuring conditions [29]. Beginning with the study of poorly soluble reactants used in low-temperature experiments, up to highest reactant concentrations possibly showing second-order kinetics [6,12,30], the mathematical tools exist for both adequate planning of experiments and kinetic classification of any system. The expressions include all limiting cases, from direct rate-based non-isothermal methods, such as TG or DTG, to adiabatic calorimetry, from low to high heating rates, from the "ideal" kinetic dilution to typically industrial, preparative reaction conditions, which often suffer from the danger of thermal explosion [5,30–34].

The necessarily empirical and approximate character of the expressions suggested should not restrict their applicability as the preferred idea is to obtain a general picture of the reaction mechanism. Systematic small deviations of S/M convergence points from the elementary position due to extraordinarily low k_∞ values can generally be tolerated. The important observation that a convergence point near to an elementary source point really exists, is not violated by such deviations. If the studies confirm an elementary process, the usual calculation procedures for correct activation data may be used. In contrast, if studies of concentration or heating-rate series result in the requirement of a definite complex mechanism, the comparable computer simulation of theoretical curves is surely an obligatory tool for the determination of the activation data of the partial steps [3,23,35,36].

Based on the variety of the systems investigated, the conclusion reached is that computer-assisted DTA is a universal means for the kinetic characterization of reactions in solution. Many relationships introduced in this area may even be applied to solid-phase experiments in commercial equipment, characterized by considerable temperature gradients inside the sample. Then, additional series have to be performed for a specific apparatus in order to develop adequate correction terms which consider sample mass, size, packing density and other technical parameters [13,14,37,38].

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