

CHARACTERISTIC TEMPERATURES OF NON-ISOTHERMAL RATE SIGNALS OF ONE-STEP PROCESSES

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Analytical expressions for the heights, and for the initial, the peak and the final temperature of the rate signals of bimolecular reactions, measured at constantly increased temperature, are derived. They are based on the specific time of the reaction, available from the activation data, and on the relative minimum rate used. DTA and non-isothermal u.v. absorption studies of 29 different organic reactions in solution reveal that the accuracy of the expressions is sufficient to reproduce the true position of peaks of one-step reactions on the temperature or time axis. A program for simple calculations, written in BASIC, is enclosed.

In the approximate kinetic theory of the author [1, 2], it is shown that the position and shape of the reaction rate peak of an elementary reaction of n -th order, generated for temperature rise proportional to time ($T = m \cdot t$), can be calculated from the activation data (E, k_{∞}) via the specific time u at the maximum,

$$u_m = \frac{E}{m \cdot R \cdot (\ln k_{\infty} + \ln u_m)^2} = \frac{m \cdot R \cdot t_m^2}{E} = \frac{RT_m^2}{m \cdot E} \quad (1)$$

using the heating rate m (deg/min) and gas constant R . For a first-order process, this theory, which may be called "Theory of the Characteristic Rate Coefficients", is based on typical products of a specific rate coefficient with the u -parameter at characteristic points of the curve (onset, halfwidth points, peak, points of inflection, end), and has been shown to be very useful for the study and discussion of non-isothermal kinetic signals. For example, for a first-order process, the rate coefficients at start, maximum and end are obtained as follows [1, 3],

$$k_0 \approx \frac{\chi}{u_m e} \quad (2a)$$

$$k_m \approx \frac{1}{u_m} \quad (2b)$$

$$k_e \approx \frac{1}{u_m} \cdot (2.82 - \ln \chi) \quad (2c)$$

using the relative minimum rate χ and the resulting maximum rate,

$$v_m \approx \frac{A_0}{e \cdot u_m} \quad (3)$$

(A_0 = initial concentration of reactant; $e = 2.718 \dots$).

From these rate coefficients and the Arrhenius equation, the characteristic times and temperatures may be calculated.

In the case of bimolecular reactions with non-equimolecular reactants, there is no elementary closed solution for these rate coefficients. Therefore, we had developed an empirical formula for the rate at the maximum, based on computer simulations [4, 5],

$$k_m \approx \frac{d}{u_m \cdot A_0^a \cdot B_0^b} \text{ with } a \approx 0.19, b \approx 0.75, d \approx 1.15, \text{ if } A_0 < B_0 \quad (4)$$

Although this expression is, for many operations, a satisfactory approximation, it is neither exact nor really understandable, as can be seen from the lack of exchangeability of the reactants, A and B . Therefore, we have elaborated a better founded procedure, which is directly based on the rate law.

Theory

We consider a reaction of the type $A + B = \text{product(s)}$, characterized by the rate law

$$-\frac{dA}{dt} = k \cdot A \cdot B = k \cdot A(B_0 - A_0 + A) \quad (5)$$

using notations A_0, B_0 as starting concentrations and the abbreviation

$$\int_0^t k \, d\zeta = \int_0^t k_\infty \cdot \exp[-E/(R \cdot m \cdot \zeta)] \cdot d\zeta = (uk)_t, \quad (6)$$

and assuming $B_0 > A_0$. After rearrangement of the variables, we obtain

$$\begin{aligned} (B_0 - A_0) \int_{A_0}^{A_t} \frac{dA}{A(B_0 - A_0 + A)} &= \int_{A_0}^{A_t} \frac{dA}{A} - \int_{A_0}^{A_t} \frac{dA}{B_0 - A_0 + A} = \\ &= -(B_0 - A_0) \cdot (uk)_t \end{aligned} \quad (7)$$

and integration yields

$$\ln \frac{A_t}{A_0} - \ln \frac{B_0 - A_0 + A_t}{B_0} = \ln \left[\frac{A_t}{A_0} \cdot \frac{B_0}{B_0 - A_0 + A_t} \right] = (A_0 - B_0) \cdot (uk)_t \quad (8)$$

and, after exponentiation,

$$\frac{A_t}{A_0} \cdot \frac{B_0}{B_0 - A_0 + A_t} = \exp [(A_0 - B_0) \cdot (uk)_t] \quad (9)$$

Then, the concentration shows the time dependence

$$A_t = A_0 \cdot \frac{(B_0 - A_0) \cdot Z_t}{B_0 - A_0 \cdot Z_t} \quad (10)$$

where

$$Z_t = \exp [(A_0 - B_0) \cdot (uk)_t] \quad (11)$$

The current rate is given by insertion of A_t into Eq. (5) and some rearrangements,

$$v_t = - \frac{dA}{dt} = A_0 \cdot B_0 \cdot (B_0 - A_0)^2 \cdot \frac{k_t \cdot Z_t}{(B_0 - A_0 \cdot Z_t)^2} \quad (12)$$

and for the pseudo-unimolecular case ($B_0 \rightarrow \infty$),

$$v_t = A_0 B_0 k_t Z_m \quad (12a)$$

In order to find the time for the peak maximum, the time derivative of v_t has to be equated to zero. To do this, we neglect the temperature dependence of $u(t)$ *, which is only ca. 20% over the total time range passed through, compared to the dramatic changes of the rate coefficient (ca. 5 orders of magnitude for second order, 3.5 for first order). Thus,

$$\begin{aligned} \frac{dk_t}{dt} &= \frac{d \left[k_\infty \exp \left(- \frac{E}{mRt} \right) \right]}{dt} = \\ &= \frac{E}{mRt^2} k_\infty \exp \left(- \frac{E}{mRt} \right) \approx \frac{k_m}{u_m} \end{aligned} \quad (13)$$

* This is a fundamental simplification in the Theory [1].

may be assumed (cf. Eq. (1)). The rate in Eq. (12) is proportional to the ratio of two time-dependent functions, U and V ,

$$U = k_t \cdot Z_t \quad (14a)$$

$$V = (B_0 - A_0 \cdot Z_t)^2 \quad (14b)$$

Forming the derivative, one obtains

$$\frac{dU}{dt} = \left[\frac{1}{u_m} + (A_0 - B_0)k_t \right] \cdot k_t \cdot Z_t \quad (15a)$$

$$\frac{dV}{dt} = -2A_0(A_0 - B_0)(B_0 - A_0Z_t) \cdot k \cdot Z_t \quad (15b)$$

Since

$$\frac{dv_t}{dt} = \frac{VU' - UV'}{V^2} = \emptyset, \quad (15c)$$

and V^2 is different from zero, we have

$$\begin{aligned} VU' - UV' = & -2A_0(A_0 - B_0) \cdot k_m \cdot Z_m - A_0 \left[\frac{1}{u_m} + (A_0 - B_0)k_m \right] \cdot Z_m + \\ & + \left[\frac{1}{u_m} + (A_0 - B_0)k_m \right] B_0 = \emptyset \end{aligned} \quad (16)$$

where index m denotes the corresponding values at the maximum of v_t . Hence, the following expression is obtained,

$$\begin{aligned} A_0 \cdot Z_m - \frac{A_0}{u_m} \cdot [1 + (A_0 - B_0)(uk)_m] \cdot Z_m + \\ + B_0 \cdot \left[\frac{1}{u_m} + (B_0 - A_0)(uk)_m \right] = \emptyset \end{aligned} \quad (17)$$

and, finally,

$$(uk)_m = \frac{1}{B_0 - A_0} \cdot \frac{\frac{B_0}{A_0} Z_m - 1}{\frac{B_0}{A_0} Z_m + 1} \quad (18)$$

As Table 1 reveals, this expression for $(uk)_m$ (and, similarly, $(uk)_e$; see Eq. (23)) converges rapidly for any assumed uk starting values, for example $(uk)_a = 1/(B_0 - A_0)$ (Table 1). In practice, 5–7 iteration steps are mostly sufficient. Then, the rate coefficients at the onset and at the end of the signal (relative minimum rate = χ) are available using the rate coefficient k_m ; at onset,

$$\chi = \frac{v_0}{v_m} = \frac{A_0 B_0 k_0}{A_m B_m k_m} = \frac{A_0 B_0 k_0}{A_m (B_0 - A_0 + A_m) \cdot k_m} \quad (19)$$

$$k_0 = \chi \cdot k_m \cdot A_m \cdot \frac{B_0 - A_0 + A_m}{A_0 \cdot B_0} \quad (20)$$

using

$$A_m = A_0 \frac{(B_0 - A_0) \cdot Z_m}{B_0 - A_0 \cdot Z_m} \quad (21)$$

(cf. Eq. (10)). Similarly, we obtain at the end (index e)

$$k_e = \chi \cdot k_m \cdot e^{(A_0 - B_0)[(uk)_e - (uk)_m]} \cdot \left[\frac{A_0 - B_0 + A_m}{A_0 - B_0 + A_e} \right]^2 \quad (22)$$

Table 1 Convergence of (uk) at signal maximum and end for bimolecular processes (cf. BASIC program)

Iteration No.	Case 1 $(uk)_m$	$(uk)_e$	Case 2 $(uk)_m$	$(uk)_e$	Case 3 $(uk)_m$	$(uk)_e$
1	9.63346	1047.74	4.26655	72.8083	1.02429	14.46970
2	9.68815	1056.51	4.34424	55.3422	1.02609	9.76339
3	9.71544	1058.10	4.36650	53.5148	1.02623	9.32629
4	9.72905	1058.38	4.37285	53.2914	1.02624	9.27542
5	9.73584	1058.43	4.37466			
6	9.73922	1058.44	4.37517			
7	9.74091		4.37532			
8	9.74175		4.37536			
9	9.74238					
10	9.74249					

Bimol. standard reaction: $E = 62.8$ kJ/mol; $k_\infty = 10^{12}$ dm³ mol⁻¹ min⁻¹

$m = 1.5$ K min⁻¹; $\chi = 0.005$; $u_m = 5.84$ min

Case 1 $A_0 = 0.1$ $B_0 = 0.105$

Case 2 $A_0 = 0.1$ $B_0 = 0.25$

Case 3 $A_0 = 0.1$ $B_0 = 1$ (Moles/L)

Starting values: $(uk)_m = \frac{1}{B_0}$; $(uk)_e = 1000$

Stop of iteration: Change of $uk < 10^{-3}\%$

and $(uk)_e$ can also be calculated iteratively, using Eqs (23) and (23a) (cf. Eq. (18)),

$$(uk)_e = (uk)_m + \frac{1}{A_0 - B_0} \cdot [\ln (uk)_m - \ln (uk)_e + \ln \chi + \ln Y^2] \quad (23)$$

where

$$Y = \frac{A_0 - B_0 + A_m}{(A_0 - B_0) \cdot \left[1 + \frac{A_0 Z_e}{A_0 Z_e - B_0} \right]} \quad (23a)$$

if Eqs (11) and (21) are analogously referred to $(uk)_e$. For $B_0 = A_0$ ("strict" second-order case), both iteration procedures reveal bad results (cf. Table 1), so that the direct second-order formulae (cf. (1)) should be preferred,

$$k_0 = \frac{\chi}{2u_m \cdot A_0} \quad (24a)$$

$$k_m = \frac{1}{u_m \cdot A_0} \quad (24b)$$

$$k_e = \frac{2}{u_m \cdot \chi \cdot A_0} \quad (24c)$$

After the iteration procedures, the corresponding rate coefficients may be obtained from $(uk)_m$ and $(uk)_e$, respectively, by division by u_m , and the characteristic temperatures by using the Arrhenius equation.

In the appendix, a simple basic program for all calculations needed for a special case is presented.

Experiments, evaluation and results

For the examination of the relationships from above, we used both theoretical signal curves, available by numerical integration [4, 7-10], and DTA and u.v.-spectrometric curves of various reactions in solution (see legend). The DTA experiments were performed in our "all-liquid"-apparatus [11], the temperature-programmed measurements of the optical density in a double-beam spectrometer with vacuum-insulated quartz cuvettes [12, 13] and an Eurotherm temperature controller.

The evaluation of the derivative u.v.-extinction difference/time curves was based on the usual bimolecular rate law and the Lambert-Beer law, assuming a temperature-independent extinction coefficient [3, 12]. In the case of the DTA

curves, two methods were used for obtaining the rate coefficients as a function of temperature.

1) Using the equation of Borchardt and Daniels [2, 4, 14-15].

2) Direct calculation of the rate curve from the heat flow curve using the Tian differential equation (also denoted as Newton equation or calorimeter equation ([16]) and subsequent calculation of k_t from the rate law.

Comparison of the new expressions requires the rate curve, i.e. application of the second method, whereas we generally use the first method for obtaining activation data and mechanistic coordinates (corrected shape index and reaction type index [3, 10]) from our experiments (cf. Fig. 1).

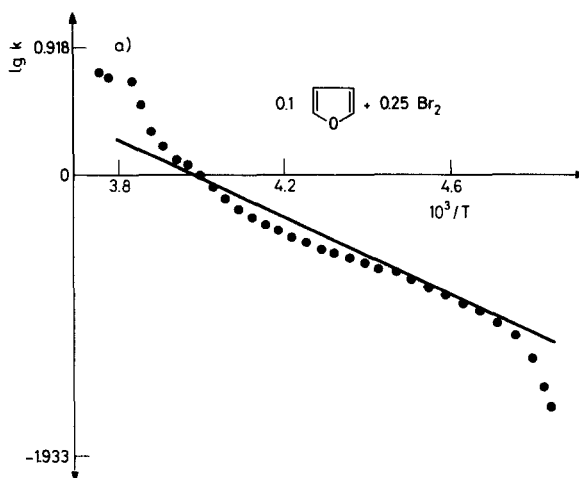


Fig. 1 Example for the different evaluation techniques, applied to a bimolecular DTA experiment System B6 (cf. Table 4b): 0.1 M furan + 0.25 M bromine, solved in methylene chloride + 10% ethanol to 5 cm³.

Heating rate: 0.77 deg/min; cell constant and heat capacity at maximum: 0.142 min⁻¹; 2.84 cal/K; maximum temperature: difference: 0.380 K; $-\Delta H = 68.8$ kJ/mol

Fig. 1a/b Borchardt-Daniels evaluation of the DTA curve and Arrhenius plot yielding

$$E = 35.7 \text{ kJ/mol}, \log k_{\infty} = 7.21; \theta_m = 0.380 \text{ K}$$

Fig. 1a $\log k$ vs. $1/T$; exp. values; — fitted straight line

A further test of the accuracy of the resulting activation parameters is the direct theoretical reproduction of the DTA curves, using the activation data, obtained by either evaluation path 1) or 2). It is obvious that a rate curve (Fig. 1d), because of its derivative character, reveals much stronger fluctuations than a DTA curve. With view to the Tian heat balance equation, the character of the DTA curve is between integral (cell constant is zero), and differential (cell constant is infinite) [17-19]. Hence, an accurate determination of shape index and halfwidth from the rate

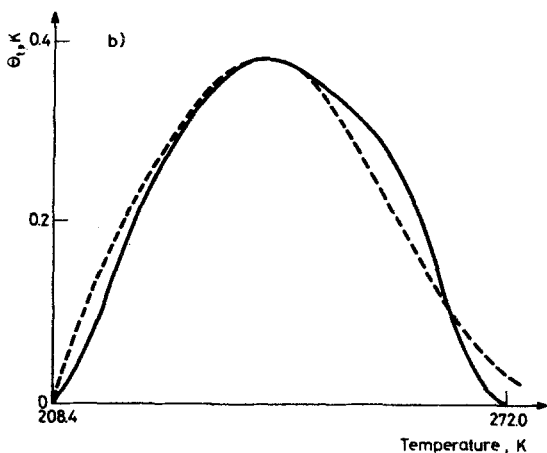


Fig. 1b Smoothed experimental (—) or theoretical (---) DTA curve assuming a bimolecular process and activation data from above

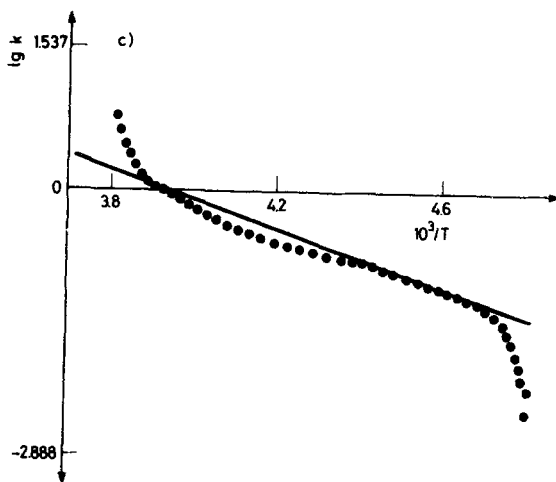


Fig. 1c/d Calculation of the rate curve from the DTA curve and Arrh. plot yielding $E = 28.1$ kJ/mol, $\lg k_{\infty} = 5.59$, $v_m = 0.0020$ dm³/mol·min

Fig. 1c $\log k$ vs. $1/T$

curves, which do not involve the thermal lag effect, but involve the heat feedback effect, seems more difficult than from the DTA curves. Nevertheless, the resulting activation parameters agree well [16].

Table 2 shows the characteristic rate coefficients and temperatures obtained for some simulated rate curves, compared with the values calculated from the

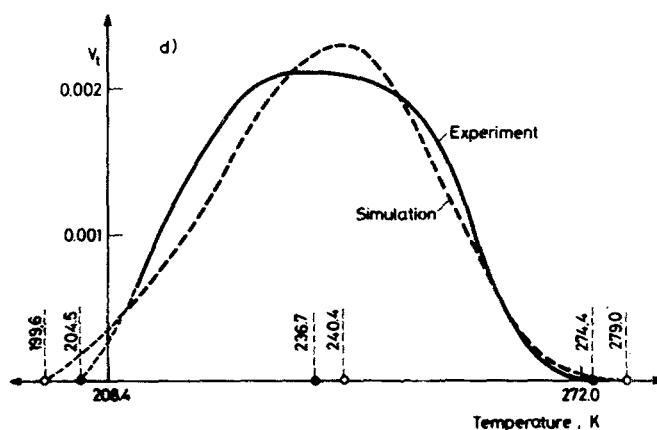


Fig. 1d Smoothed rate curve and theoretical bimolecular rate curve using the data from above; extrapolation of limit temperatures; peak temperatures

Table 2 Characteristic temperatures for some theoretical rate curves

	E	$\lg k_\infty$	m	A_0	B_0	$10^3 \cdot k_0$	k_m	k_e	T_0	T_m	T_e	v_m
<i>First-order type $A \rightarrow \text{products}(s)$</i>												
T1	62.8	12	1.5	(0.01)	—	a) 0.30	0.180	1.40	212.1	259.4	279.0	$6.67 \cdot 10^{-4}$
						b) 0.314	0.171	1.40	212.2	257.7	277.9	$6.30 \cdot 10^{-4}$
<i>Bimolecular type $A + B \rightarrow \text{products}(s)$</i>												
T2	62.8	12	1.5	0.001	0.0035	a) 6.30	35.0	380	250.5	316.4	351.0	$4.20 \cdot 10^{-5}$
						b) 8.30	52.1	559	251.4	320.4	355.5	$5.80 \cdot 10^{-5}$
T3	62.8	12	1.5	0.01	0.20	a) 2.50	0.78	6.00	226.5	273.2	295.8	$5.95 \cdot 10^{-4}$
						b) 1.60	0.87	7.55	222.1	272.7	295.8	$6.21 \cdot 10^{-4}$
T4	62.8	12	1.5	0.2	0.55	a) 0.80	0.32	3.50	219.0	264.8	288.8	$1.15 \cdot 10^{-2}$
						b) 0.51	0.34	3.90	215.1	263.8	288.4	$1.12 \cdot 10^{-2}$
T5	41.9	13	0.5	0.10	0.17	a) 0.79	0.66	12.0	145.0	179.0	209.0	$1.98 \cdot 10^{-3}$
						b) 0.91	0.67	10.4	136.7	166.4	183.5	$3.10 \cdot 10^{-3}$
T6	41.9	13	1.5	0.10	0.17	a) 2.40	0.48	34.0	141.0	165.5	190.0	$8.10 \cdot 10^{-3}$
						b) 2.70	1.99	32.5	140.8	172.7	190.7	$8.60 \cdot 10^{-3}$
T7	41.9	13	5.0	0.10	0.17	a) 11.0	5.40	84.0	149.0	179.5	198.5	$2.51 \cdot 10^{-2}$
						b) 8.3	6.2	100.0	145.4	179.6	198.6	$2.66 \cdot 10^{-2}$

Assumed relative minimum rate: $\chi = 0.005$

Units: kJ, mol, min and K. Rate constants: unimol. min^{-1} ; bimol. $\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$

a) data of simulated rate curve

b) data from Eqs (2a-c), (18), (23) respectively

The corresponding DTA signal heights, halfwidths, shape indices etc. which were calculated using the "uc-theory" [17] will be presented in another publication for all examples.

equations presented, when a relative minimum rate of $\chi = 0.005$ (0.5%) is assumed. Then, these temperatures nearly reflect the true values: The rate coefficients usually differ from theory by a factor below 1 : 1.5, corresponding to less than 2% of the total temperature range passed through by the experiment.

Apart from the u.v. extinction measurements (Table 3), the DTA-curve of three types of systems were evaluated: of nearly first-order type (examples in Table 4a), of bimolecular type (Table 4b), and of complex type (Table 4c). This classification is based on the values of the mechanistic coordinates [3, 10].

Table 3 Test of the "Theory of Characteristic Rate Coefficients" by some UV-experiments

	A_0	B_0	m	u_m	E	$\lg k_\infty$	S	$10^4 \cdot M$	T_0	T_m	T_e
U1	.00023	.00113	1.42		b) 91.6	17.75	1.07	176	271.3	296.8	321.0
				4.32	c) same		0.69	(172)	278.0	310.0	328.7
					d) 91.6	18.42	0.69		267.0	297.3	316.3
U2	.0005	.00375	1.45		b) 76.9	15.21	0.73	181	260.6	287.8	305.0
				4.78	c) same		0.65	(180)	264.8	299.6	318.4
					d) 76.9	15.71	0.70		259.7	288.0	305.9
U3	.0025	.00025	1.11		b) (213.9)	(40.68)	0.74	170	298.8	309	318.2
				2.59	c) same		1.12	(123)	286.5	296.4	297.2
					d) 167.5	30.55	0.62		≈295	309	319.2
U4	.0093	.448	1.59		b) 95.9	16.38	0.45	156	271.5	298.6	309.2
				4.71	c) same		0.69	(172)	272.0	301.0	315.1
					d) 95.9	16.66	0.67		267.1	295.3	310.9
U5	.094	.17	1.65		b) (226.9)	(42.3)	0.85	137	275.5	284.4	289.7
				1.65	c) same		0.89	(144)	272.7	284.9	291.9
				double peak	d) 159.1	29.97	≈0.72		269.5	282.3	≈293
U6	.00112	.19	1.63		b) 42.5	≈7.55	0.48	187	227.0	282.0	316.0
				8.26	c) same		0.58	(194)	234.5	287.1	318.4
					d) 42.5	7.67	0.71		219.0	282.5	316.0
U7	.0004	.00244	1.53		v) 32.9	7.50	0.91	455	266.1	282.0	306.4
				7.03	c) same		0.67	(177)	230.4	301.9	351.5
				very complex	d) 32.9	7.60	≈0.70		≈243	281.5	≈321
U8	.00025	.0006	1.09		b) 59.9	12.53	0.4/1.4	134	268.0	289.5	316.0
				6.99	c) same		0.81	(154)	262.9	310.4	341.1
				two overlapped peaks	d) 59.9	12.63	0.78		≈261	296.8	326.3
U9	.00025	.0003	1.08		b) 87.4	17.37	0.60	234	272.3	311.5	326.0
				5.60	c) same		0.62	(127)	278.0	314.1	346.0
				two overlapped peaks	d) 87.4	17.77	1.00		267.1	278.2	354.5
U10	.096	.14	1.70		b) 91.4	16.01	1.43	193	274.9	289.3	317.0
				4.40	c) same		0.96	(136)	271.3	303.7	327.0*
				second, much smaller peak	d) 91.4	16.75	≈0.92		265.9	290.3	315.6

Legend for Tables 3 and 4a-c (Cf. Table 2)

A_0, B_0 = initial concentrations of reactants; E = activation energy; k_∞ = preexp. factor; M = reaction type index; S = shape index; noise level; .05

a) Data from the equation of Borhardt and Daniels [14]

b) Data from the rate curve (after transformation in the case of DTA)

c) Application of expressions 2a-c or 18, 23 and 24, respectively

d) Data from fitted theoretical DTA-curve or rate curve (Fig. 3)

Systems:

Table 3:

U1-U2 $\text{Ce}(\text{SO}_4)_2$ + malonic acid in 1.25 m aq. sulfuric acid

U3, U7-U9 $\text{Ce}(\text{SO}_4)_2$ + tartronic acid in 1.25 m aq. sulfuric acid

U4, U5, U10 Diacetyl + H_2O_2 in H_2O

U6 Isobulylidene-indandione + 1,1-dimethoxy-ethene in toluene.

Table 4a-c Test of the "Theory of Characteristic Rate Coefficients" by some example DTA experiments (cf. legend)

(Table 4a) Unimolecular cases

	A_0	m	u_m	E	$\lg k_\infty$	S	$10^4 \cdot M$	T_0	T_m	T_e
D1	0.055	1.50	4.38	a) 64.3	12.36	0.60	205	229.3	261.6	259.4
				b) 81.4	16.27	0.78		229.3	253.3	272.2
				c) same		(0.57)		232.6	256.5	268.7
				d) _r 81.4	16.45	0.54		227.2	255.1	269.5
D2	0.1	0.711	9.64	a) 120.8	18.72	0.59	206	293.3	325.9	343.1
				b) 123.2	19.11	0.56		293.3	321.1	338.3
				c) same		(0.57)		295.6	321.1	333.9
				d) 123.2	19.23	0.70		289.9	321.1	336.5
D3	0.3	1.56	5.02	a) 116.6	18.21	0.52	182	298.0	331.0	354.0
				b) 116.6	17.29	0.79		296.1	324.6	342.0
				c) same		(0.57)		296.3	324.9	339.4
				d) 116.6	17.42	0.66		293.9	324.1	341.2
D4	0.2	2.25	3.01	a) 124.9	19.79	≈ 0.45	203	299.9	337.0	363.7
				b) 128.9	20.30	0.62		298.3	326.5	344.8
				c) same		(0.57)		299.9	325.0	337.5
				d) 128.9	20.30	0.65		297.9	326.7	340.2
D5	0.2	0.487	18.11	a) 93.4	14.14	0.49	210	290.4	326.1	338.9
				b) 89.3	13.32	0.61		288.0	319.8	337.0
				c) same		(0.57)		286.0	320.0	337.8
				d) 98.9	15.02	0.67		284.7	319.7	337.9
Theory:						0.58	199			

Table 4a:

D1 $(\text{PhO})_3\text{PO}_3$ in CH_2Cl_2

D2 Ph-N=N-OH in 2 m aq. HCl

D3-D5 Ph-N=N-OH in 2 m sulfuric acid.

(Table 4b) Bimolecular cases

	A_0	B_0	m	u_m	E	$\lg k_\infty$	S	$10^4 \cdot M$	T_0	T_m	T_e
B1	0.25	0.25	1.55	5.59	a) 50.0	10.70	0.57	136	214.9	259.1	281.7
					b) 51.6	10.88	1.06	(125)	214.9	246.9	276.4
					c) same		1.14		213.9	238.5	286.7
					d) same		1.09		207.6	244.2	282.9
Type 2											
B2	0.10	0.10	0.86	6.66	a) 82.5	16.70	1.49	150	245.2	268.9	290.5
					b) 89.6	18.04	1.42	(123)	≈243.0	260.2	289.9
					c) same		1.14		241.0	258.2	289.9
					d) 89.6	18.00	1.29		239.6	262.1	293.9
Type 2											
B3	0.364	0.457	1.68	5.83	a) 56.0	11.12	0.71	139	200.0	237.0	272.0
					b) 42.6	9.18	0.98		196.0	230.3	254.1
					c) same		1.02	(129)	194.7	233.2	269.1
					d) 58.2	13.05	1.04		196.0	229.3	256.6
Type AB											
B4	0.055	0.075	1.51	4.53	a) 72.1	15.39	0.60	158	219.1	265.5	287.7
					b) 68.8	14.46	0.63		219.1	256.5	282.0
					c) same		0.99	(133)	227.3	258.1	291.5
					d) 68.9	14.49	0.96		216.5	257.9	284.4
B5	0.015	0.025	1.53	5.58	a) 55.2	11.41	0.71	174	258.4	283.3	329.5
					b) 58.0	11.69	≈1.73		253.5	273.4	307.4
					c) same		0.91	(141)	240.3	281.8	312.0
					d) 58.0	11.89	0.98		245.2	379.2	311.8
B6	0.10	0.25	0.77	14.98	a) 28.1	5.59	0.95	188	208.4	236.3	272.0
					b) 35.7	7.21	0.63		204.5	236.7	274.4
					c) same		0.80	(155)	195.2	241.2	273.2
					d) same		0.79		199.6	240.4	279.0
B7	0.17	1.0	1.84	7.50	a) 37.0	8.16	0.83	212	182.3	228.7	260.7
					b) 37.7	8.40	0.80		183.1	223.7	241.2
					c) same		0.67	(176)	181.0	216.2	237.3
					d) 39.8	8.87	0.75		179.6	224.6	241.7
B8	0.04	0.83	1.60	7.56	a) 88.1	12.41	0.59	183	316.0	359.9	374.1
					b) 83.9	11.69	0.80		315.0	349.3	371.1
					c) same		0.60	(189)	309.3	352.5	375.6
					d) 83.9	11.74	0.65		310.0	350.0	372.3
B9	0.78	22.4	1.73	9.95	a) 63.1	9.17	0.55	172	251.3	294.3	322.8
					b) 53.6	7.42	0.54		248.8	288.3	311.9
					c) same		0.60	(191)	244.1	287.7	312.3
					d) 60.7	8.98	0.68		246.1	287.3	312.0
theory Type 2							1.14	132			
AB							0.58-1.14	132-199			

Table 4b: B1, B6 Furan + bromine in CH_2Cl_2 + 10% ethanol
 B2 Maleinic acid anhydride + furan in toluene

- B3 $(\text{PhO})_3\text{PO}_3$ + 2,3-dimethylbutene-(2) in CH_2Cl_2
 B4 $(\text{PhO})_3\text{PO}_3$ + cyclohexadiene-(1,3) in CH_2Cl_2
 B5 $\text{Ce}(\text{SO}_4)_2$ + malonic acid in 1.25 m aq. sulfuric acid
 B7 cis-cyclooctadiene-(1,5) + cyclopentadiene-(1,3) in toluene
 B8 Ozone + diisopropylether in CH_2Cl_2
 B9 Benzoylchloride in methanol.

(Table 4c) Complex Cases

	A_0	B_0	m	u_m	E	$\lg k_\infty$	S	$10^4 \cdot M$	T_0	T_m	T_e	
C1	0.0005	0.00345	1.62	9.69	a) 22.9	4.57	2.99	299	267.0	301.6	348.9	
				third component:	9.72	b) 30.2	5.62	0.78		258.5	294.1	346.6
				0.025		c) same		0.66	(178)	229.5	308.7	365.8
						d) same		0.71		241.6	299.8	353.4
C2	0.03	0.0675	1.44	14.03	a) 22.6	3.79	0.73	209	266.9	348.0	368.8	
				14.03	b) 28.7	4.54	0.54		263.4	340.3	366.7	
					c) same		0.82	(152)	238.3	336.1	424.5	
					d) same		0.90		247.2	321.7	393.4	
C3	0.05	0.05	1.56	4.63	a) 81.6	15.12	0.86	117	274.2	309.6	340.6	
				4.63	b) 87.8	15.95	1.47		272.4	293.0	338.3	
					c) same		1.14	(124)	272.0	294.6	338.5	
					d) same		1.00		267.3	298.7	342.0	
C4	0.08	0.587	1.58	5.91	a) 111.6	16.63	0.42	181	306.4	350.1	367.8	
				5.91	b) 100.2	14.85	0.65		303.0	341.2	363.1	
					c) same		0.65	(179)	306.1	341.3	360.0	
					d) same		0.71		300.5	342.2	364.4	
C5	0.08	1.0	1.62	5.09	a) 114.4	18.73	0.37	249	283.5	319.1	342.4	
				5.09	b) 95.6	15.52	0.59		280.7	309.9	323.5	
					c) same		0.62	(185)	278.6	308.7	324.3	
					d) same		0.77		277.4	311.1	328.0	
C6	0.03	0.95	0.52		a) 40.1	7.50	0.70	221	207.6	242.6	263.9	
				22.41	b) 39.9	7.48	0.80		203.7	233.8	261.6	
					c) same		0.59	(191)	198.3	237.6	260.3	
					d) 39.9	7.58	0.73		198.7	235.6	262.7	
C7	0.35	0.35	1.94	(6.88)	a) 40.4	7.46	3.62	150	250.4	277.1	321.5	
				5.45	b) 56.7	10.30	≈ 1.70		246.5	268.1	319.5	
					c) same		1.14	(126)	243.5	272.9	312.6	
					d) same		1.07		240.1	277.9	328.4	
C8	0.11	0.40	1.33	7.91	a) 41.2	8.25	0.97	231	215.0	246.0	285.0	
				8.00	b) 43.6	8.75	0.97		215.0	239.0	265.9	
					c) same		0.73	(166)	207.3	247.7	272.7	
					d) same		0.69		214.2	247.5	264.9	

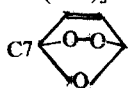
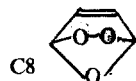
(Table 4c) cont.

	A_0	B_0	m	u_m	E	$\lg k_\infty$	S	$10^4 \cdot M$	T_0	T_m	T_e
C9	0.058	0.10	1.58	a)	24.0	5.83	0.93	226	178.6	226.9	277.6
				b)	25.3	6.02	0.73	171.7	214.6	268.7	
				c)	same		0.90 (143)	171.8	226.4	274.4	
				d)	25.3	6.17	0.96	165.6	216.1	261.1	

Table 4c:

C1 NaBrO₃ + NaBr + 0.025 m Ce(SO₄)₂ + 0.375 m malonic acid in 1.25 m aq. sulfuric acid

C2 1-(4-hydroxy)-phenyl-2-methylamine-propane in 1.5 m aq. sulfuric acid

C3 NaBrO₃ + NaBr in 1.25 m aq. sulfuric acidC4 NaIO₃ + H₂O₂ in 0.1 m aq. sulfuric acidC5 NaIO₃ + H₂O₂ + 0.001 m MnSO₄ in 0.1 m aq. sulfuric acidC6 (PhO)₃PO₃ + 2-methylbutene-(2) in CH₂Cl₂C7 CH₂NH₂ + (PhO)₃PO₃ in toluene

C8 in methanol

C9 (PhO)₃PO₃ + cyclopentadiene (1.3) in CH₂Cl₂

The starting concentrations of the first and second components are listed in the tables

The results for the initial and final rate coefficients obtained by the presented new equations reveal for these experiments that the total temperature or time interval observed is much smaller than corresponding to $\chi = 0.005$, which was appropriate for the theoretical curves. The shifts of both onset and end temperature disappear in the elementary cases if a tenfold value, $\chi = 0.05$, is assumed for the relative minimum rate. This means that the limiting points, which represent the first and the last deviation from the base line, are considerably shifted against the peak maximum, due to the thermal noise in the small temperature difference—in the range of 5/1000 K—whilst for the theoretical curves these points are determined by the optical resolution on the chart paper or terminal screen.

The evaluations were performed by programs DTA and DTAD (calculation of the rate curves) [4, 10, 16], the comparative simulations by program METEX [6], all running on a VAX 11 computer. The values stemming from the Theory of the Characteristic Rates were obtained using the BASIC program in the appendix on a SHARP PC-1350 pocket computer.

Table 5 illustrated for all 45 systems studied that using $\chi = 0.05$ indeed causes the calculated temperatures to agree with the true values within the double standard deviations. The observed deviations are, in general, not caused by bad validity of the concept of the characteristic rates; as may be seen from Tables 3–4 in detail, the main reason is that the elementary course is not accurately followed by many

Table 5 Mean values of the differences between experimental and theoretical characteristic temperatures and their standard deviations

Subject	Plots	$T_e - T_0$, K	% deviation of temperature of experiment		
			onset	maximum	end
Theoretical rate curves using integration program METEX					
unimolecular and bimolecular	7	66.6 ± 19.9	+ 1.37 ± 3.00	- 0.41 ± 1.92	- 0.96 ± 2.90
UV experiments					
elementary	3	61.2 ± 24.2	+ 0.07 ± 2.73	+ 0.51 ± 11.74	- 1.07 ± 13.71
complex	7	38.0 ± 13.1	+ 10.39 ± 43.90	- 5.37 ± 17.06	- 15.28 ± 57.48
DTA experiments					
unimolecular	10	45.8 ± 7.5	- 1.70 ± 9.60	+ 0.32 ± 3.58	+ 2.91 ± 7.80
bimolecular	19	64.8 ± 20.0	+ 5.00 ± 12.20	- 2.14 ± 6.97	- 4.68 ± 11.10
complex	16	72.1 ± 19.4	- 2.66 ± 14.59	+ 1.61 ± 23.18	- 14.49 ± 20.54

The temperature deviations, obtained from Tables 2-4, were related to the total temperature intervals $\Delta T = T_e - T_0$ of the experiments.

Then, mean and standard deviation were calculated for the respective group.

reactions, as is indicated by the discrepancies between experimental and theoretical curves (see activation data in rows b) and d)) and by the mechanistic coordinates as well.

Discussion

In non-isothermal reaction kinetics based on a temperature rise linear with time, the Theory of Characteristic Rate Coefficients [1] allows estimations of favourable experimental conditions for a given kinetic problem, even for complex processes. It should be applicable to all methods yielding rate-proportional signals, such as power-compensating DSC, DTG, EGA etc. (cf. Table 2, 4). DTA experiments in appropriate equipment may be included, as is shown by Table 4a-c.

This concept, based on characteristic products of the rate coefficient with the specific time at characteristic points of the rate curve, shows a strict analogy to the corresponding quantities in isothermal kinetics, when the specific time u is replaced by a constant rate coefficient k , and the variable rate coefficient $k(T)$ is replaced by the time $t - t_0$. For example, for the half time of an isothermal first-order curve one obtains $k(t_{\frac{1}{2}} - t_0) = \ln 2$, whereas for the non-isothermal plot the two halfwidth values for uk are $(uk)_1 = 0.25$, and $(uk)_2 = 2.8$. At the end of the observation

range, the results are $k(t_e - t_0) = -\ln \chi$ and $(uk)_e \approx 2.9 - \ln \chi$, respectively. Since such characteristic $(k\Delta t)$ - and (uk) -terms depend on the reaction order [1, 3], we cannot agree with the assumptions of Popescu and Segal [20] that the reaction order hypothesis does not influence the temperature range in which the reaction occurs. The prerequisites used by these authors for their discussion seem to be too rough, and our experiences with numerous reactions in solution (cf. [3, 16, 25]) are in contrast to their statement.

For confirmation of the assumed reaction order, the correlation coefficient is often used. However, it was observed by many authors, that this quantity is in many cases very insensitive to the reaction order, especially in heterogeneous kinetic studies, and, hence, is also considered as an inappropriate parameter for this purpose [21–23]. However, this problem is circumvented when parameters of another type, such as the mechanistic coordinates, are chosen for such decisions.

In our DTA and u.v. experiments in solution, the experiences with the correlation coefficients, applied both to the Arrhenius diagram and to the comparison with the true theoretical curve, are not so bad, when for DTA the term $\theta_m/(mu_m)$ (cf. Semenov temperature [19, 24]) characterizing the thermal feedback is not too high. In spite of this, we preferred the mechanistic coordinates for the selection and classification of our experimental examples. All true bimolecular processes have to reveal coordinates in the region *A* of the mechanistic diagram [3, 10], i.e. $0.58 < S < 1.15$ and $0.0130 < M < 0.0199 \text{ kJ mol}^{-1} \text{ K}^{-1}$. In our data bank, this *A*-region is the most frequent of the eleven regions defined, and this statement is representative of more than 2000 experiments in solution. Indeed, in solution chemistry, the bimolecular reactions are the most important elementary type, which even includes the pseudo-first- and the second-order case [4, 5], if $A_0 < B_0$ or $A_0 = B_0$, respectively. However, the kinetics of the reactions are often distorted by additional consecutive, competing or even recoupling processes, causing a shift of the mechanistic point *S* vs. *M* into other regions.

Direct evidence for the agreement between experimental and theoretical characteristic rate coefficients and temperatures at onset, maximum and end, due to Eqs 2, 18–24, is given in Table 3, on the basis of the derivatives of the plots of the extinction differences between sample and reference in the u.v. range. If we compare the relative temperature deviations with those of the DTA experiments, there is a general positive shift which can be nearly compensated for by taking a correction of +0.38 for the logarithmic *A*-factor, probably caused by a temperature inhomogeneity inside the cuvette (no stirring!).

However, it is really remarkable that also the DTA experiments, where generation of the rate curves needs the time derivative of the plots via the Tian heat balance differential equation, reveal an agreement with theory for the elementary cases (Table 5), comparable to the u.v.-experiments. The true temperatures are

generally within the double standard deviation. The smallest deviations appear for first order; for bimolecular cases, they are increased by 35–50% whilst the complex cases reveal deviations increased by factors of 2 to 4 or even more.

For one-step reactions, it is evident that the reproduction of the peak temperature is the best, whereas the other temperatures at the noise level must show larger errors. Further, the deviations for second order must be higher than for first order: Then, the correctness of the assumption of a constant u parameter in Eq. (13) is more violated for the total temperature interval because the latter, for the same activation parameters and a 1 : 1 molar ratio of the reactants, is ca. 150% of the first-order interval.

However, Table 5 also shows that even for bimolecular reactions it seems to be often difficult to recognize the first deviation of the DTA curve from the base line. The initial temperatures show an average positive shift of ca. 5 percent. One reason may be the argument from above that the second-order peaks are considerably broader and smaller than the first-order peaks, so that the onset becomes more indistinct. Further, some reactions start at temperatures very near to the freezing point, so that the true onset could only roughly be estimated [13, 25].

Nevertheless, the considerable difference in the agreement between elementary and complex processes remains. The tests with elementary systems confirm the theory very satisfactorily, whereas complex systems cause a dramatic increase of the standard deviations, especially for peak temperature and final temperature. This fact signals very different types of complexity; on the other hand, the predominating strong negative shift of the final temperatures means that, for the systems presented here, the net activation energies will be mainly higher than for the data of comparable true elementary processes. Then, half width and signal width will be reduced [26–27], but the reaction type indices M will be increased (Tables 3, 4c). Due to our experiences with experiments and simulations, this should rather indicate complex mechanisms of more than two steps, involving intermediates with feedback capability, or catalytic or autocatalytic reactions, than simple mechanisms consisting of parallel or consecutive reactions.

In conclusion, the Theory of Characteristic Rate Coefficients is a readily applicable approximation concept for researchers working in mass-action kinetics. If a system is studied at temperatures rised proportional to time, this theory allows to survey the reaction from a relatively simple level, circumventing the very complex exact mathematics by using the definition of a constant specific time and specific temperature difference of an elementary process as an approximation. Since the most complex mechanisms should be composed from elements of the bimolecular type, the possibility of a simple preliminary calculation of the rate coefficients and temperatures at onset, maximum and end, of the maximum signal height and even

of the maximum temperature difference in DTA* opens the way to a better planning of non-isothermal experiments and a better understanding of the results.

* * *

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Zusammenfassung — Analytische Ausdrücke werden abgeleitet, die für einen bimolekularen Prozeß die Höhe, Anfangs-, Peak- und Endtemperatur des für linear ansteigende Temperatur gemessenen Reaktionsgeschwindigkeitssignals wiedergeben. Diese basieren auf der spezifischen Zeit der Reaktion, die aus den Aktivierungsdaten und der Heizrate zu berechnen ist, und der relativen Minimalrate. DTA-

* The respective formula, presented in [17], can easily be extended for bimolecular processes; work in preparation.

und nichtisotherme UV-Absorptionsmessungen von 29 verschiedenen organischen Reaktionen beweisen, daß die Genauigkeit der Ausdrücke ausreicht, um die Lage der Signale von Einstufenreaktionen auf der Temperatur- oder Zeitachse zu beschreiben. Ein BASIC-Programm für einfache Vorausberechnungen ist beigelegt.

Резюме — Выведены аналитические выражения для высот, а также для скорости сигналов начальной, пиковой и конечной температур бимолекулярных реакций, проведенных при постоянно увеличивающейся температуре. Эти выражения основаны на специфическом времени реакции, доступном из данных кинетики реакций и на используемом уровне шума. ДТА и неизотермическое УФ спектроскопическое исследование 29 различных органических реакций в растворе показали, что точность выведенных выражений является достаточной, чтобы воспроизвести истинное положение пиков одноступенчатых реакций на температурной или временной координате. На языке Бейсик представлена программа для простых вычислений.

**Program for the pre-calculation of non-isothermal rates,
rate coefficients, times, temperatures and other data
for pocket computer SHARP PC-1350**

Input data: Activation energy kcal/mol, $\lg A$ factor (unit: min), heating rate, noise level, iteration level, initial concentrations REACTIONS: $n \cdot A \rightarrow \text{product(s)}$ (n th order) and $A + B \rightarrow \text{product(s)}$

Selection by input of reaction order n ; $n = 2$ and inequality of AO and BO means bimolecular type.

DEF A = New activation data and heating rate \Rightarrow calculation of U_m

DEF B = New starting concentrations and reaction order

\Rightarrow calculation of $v_m, A_m, k_0, k_m, k_e, t_0, t_m, t_e, T_0, T_m, T_e$, halfwidth, shape index, ratio k_e/k_0 , interval width $T_e - T_0$; next data: put "enter"

For "special situation": Input: Temperature T or time t , output: rate $v(t)$ and relative concentration (%)

Inputs line 640: V = repetition of value display; C = other concentrations; S = repetition of special situation; I = other order or iteration barrier

A) Calculation of specific time and temperature

```
10 "A": CLEAR: M=1.5: WAIT 1
20 R=.00198: U=10/M: AB=1: PRINT=LPRINT
30 INPUT "Activation energy="; E
40 IN. "logA="; F
50 IN. "heating rate="; M
60 PRINT USING "###.##"; "Activ. energy="; E: PR. "A-factor="; F:
   PR. "Heating rate="; M
```

```

70 UA=U: U=E/(M*R*(F*LN10+LNU)^2)
80 UZ=ABS((U-UA)/U): IF UZ<.0001 THEN 100
90 J=J+1: GOTO 70
100 W=M U: PR.US. "###"; J; "times"; US."###.##"; "U="; U

```

B) Characteristic rate constants, times, temperatures etc.

```

110 "B": IN. "AO="; A
120 B=O: IN. "BO(> AO)="; B
130 AB=1: IF B=O LET B=A
140 IF B=A LET B=A+.00001: AB=O
150 KX=LN((EXP1*(B/A-1)+1.6)/(B/A+.6))
160 IN. "Order="; N
170 X=.005: IN. "Noise level% (0.005)="; X
180 DK=A-B: WAIT1: AF=1
190 IF N=1 LET AB=Ø
200 IF N=2 AND AB=1 GOSUB 1100: GOTO300           Second order
210 IF N>1 GOSUB 1500: GOTO 300
220 VM=A/EXP1/U: KØ=X/EXP1/U: KM=1/U: KE=(2.9-LNX2)/U
                                                    First order

230 AM=A/EXP1: KH=KM
300 KK=KØ: GOSUB 1000: TØ=T                       Char. Temperatures
310 KK=KM: GOSUB 1000: TM=T
320 KK=KE: GOSUB 1000: TE=T
330 LQ=2.25*N^2: H=LQ*W                           Further data
340 IF AB=Ø LET UK=U*KM
350 QK=KE/KØ: TQ=W*LN QK
360 S=N^2*(1.502+.21*(N-1))/(N^2+1.59)
370 IF N<2 THEN 400
380 AF=((F+LOG U)/(F+LOG U-LOG UK))^2           Mechanistic coordin.
390 S=.58*KX+1.15*(1-KX): H=W*(2.25*KX+3.7*
(1-KX))*AF: TQ=3*H
400 MM=E/H/(F-LOGKH)^2

```

C) Displays

```

410 US. "###^"; PR. "AØ="; A; "BØ="; B; US. "###"; "Order="; N
420 PR.US. "###^"; "Max. rate="; VM; "at conc."; AM: GOSUB 2000
430 PR. "k-values (start-peak-end)"
440 PR.US. "###^"; KØ; KM; KE: GOSUB 2000
450 PR.US. "#####"; "Temperatures:"

```

```

460 PR. T∅; TM; TE; "K": PR. " ": GOSUB 2000
470 PR.US. "####.#"; "Times: ": Z∅ = T∅/M: ZM = TM/M: ZE = TE/M
480 PR.Z∅; ZM; ZE: PR. " ": GOSUB 2000
490 PR.US. "####.#"; "h="; H; " S="; S
500 PR. " ": GOSUB 2000
510 PR.US. "#.#^"; "k-ratio="; QK; " T-range="; TQ

```

D) Special situation

```

520 G$ = " ": IN. "Special situation (=S)?" ; G$
530 IF G$ = " " THEN 640
540 T = ∅: IN. "T="; T
550 Z = O: IF T = ∅ IN. "t="; Z
560 IF T = ∅ LET T = Z*M
570 K = 10^F*EXP(-E/R/T): IF N = 1 LET AT = A*EXP(-U*K): GOTO
    620
580 AT = (A^(1-N) + N*(N-1)*U*K)^(1/(1-N))
590 IF AB = ∅ THEN 620
600 AT_ = -A*DK*EXP(DK*U*K)/(B - A*EXP(DK*U*K))
610 V = K*AT*(B - A + AT): GOTO 630
620 V = AT^N*K^N
630 AP = 100*AT/A: PR.US. "#.### ": "v="; V; US. "####.#"; AP; "%A"
640 G$ = " ": IN. "Values, Conc, Spec, End, Iter?"; G$
650 IF G$ = "S" THEN 530
660 IF G$ = "E" STOP
670 IF G$ = "C" THEN 110
680 IF G$ = "V" THEN 420
690 IF G$ = "I" THEN 160
700 END

```

SUBROUTINES

Temperatures/times from Arrhenius equation

```

1000 T = E/R/(F*LN 10 - LN KK)
1010 RETURN

```

AB-case, different concentrations

```

1100 IN = ∅: N = ∅: SS = .01: IN. "Iteration barrier % (0.01)?" ; SS
1110 UK = 1/B

```

```

1120 UU = UK : IN = IN + 1
1130 UK = (1/DK)*((A/B)*EXP (DK*UK) - 1)/((A/B)*EXP (DK*UK) + 1)
1140 TQ = ABS ((UK - UU)/(UU + .00001))
1150 IF TQ > SS THEN 1120
1160 KM = UK/U : KH = KM
1170 ZZ = EXP (DK*UK)
1180 AM = -A*ZZ*DK/(B - A*ZZ)
1190 VM = KM*AM* (B - A + AM)
1200 KØ = X*KM*AM* (B - A + AM)/A/B
1210 UE = 1E2
1220 UV = UE : SU = ((B - A*EXP (DK*UE))/(B - A*EXP (DK*UK))) ^ 2
1230 UV = UE : JN = JN + 1 : UE = UK + (LN UK - LN UE + LN X + LN
    SU)/DK
1240 IF (ABS (UE - UV))/UV > SS THEN 1220
1250 KE = UE/U
1260 RETURN

```

Call for other values

```

2000 G$ = " " : IN. Cont ( ), Rep, End?"; G$
2010 IF G$ = "E" THEN 520
2020 IF G$ = "R" THEN 420
2030 RETURN

```

n-th order; equal concentrations

```

1500 KM = 1/U/A ^ (N - 1)/N : KØ = X*KM : KE = N ^ (N - 1)/((N - 1) ^ N)
    /U/(X*A) ^ (N - 1) : KH = X*KM
1510 AM = A*N ^ (1/(1 - N)) : CM = N*KM*AM ^ N
1520 RETURN

```