Journal of Thermal Analysis, Vol. 38 (1992) 1653-1669

THE 'THEOREM OF COMMON KINETIC RUNS' IN HOMOGENEOUS NON-ISOTHERMAL REACTION KINETICS

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(Received November 11, 1991)

The kinetic features of the fundamental homogeneous two-reaction models for linearly increasing temperature have been studied systematically by the analysis of 2500 signal curves (organized in 250 series), obtained from computer simulations and compared with numerous TA experiments.

For methods based on a proportionality between the particular reaction rates and their contribution to the derivative overall signal, it has been found that characteristic *behaviour sets* of three order-dependent parameters which refer to definite intervals of the starting concentration in series, can be extracted from the halfwidth and shape index of the curves. Such thermoanalytical patterns agree with those obtained from the distribution lists of some thousand DTA- and UV-experiments. They are presented for the 21 most important two-step model and almost independent of the activation data and of the method-dependent proportionality factors. Therefore, they allow for the direct kinetic identification of the complex reaction involved.

Keywords: experiments in solution, kinetic models, linear temperature program, numerical integration

Introduction and informative kinetic parameters

A long-standing aim of the kinetics of complex reactions has been the ability to identify the type of kinetic model from experimentally observed signal curves, obtained with a variation of the concentration of a suitable starting component. Undoubtedly, it would be very helpful for the kineticist, if experimentally available parameters or parameter sets would exist which – independently of the activation parameters – describe the prevailing kinetic model; this desirable situation is called 'Theorem of Common Kinetic Runs'. Using this concept, it was

John Wiley & Sons, Limited, Chichester
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shown for example that the reaction of ceric sulphate (= A) with malonic acid (= B) in dilute sulfuric acid reveals the dominant two-step models GAB1, P2T and 1KAT (see later) [1], i.e. a participation of a prereactive equilibrium ($A+B \rightleftarrows C$) and of a repeated recoupling reaction (P2T) of the ceric salt with subsequently formed reaction products (which may pretend a catalytic reaction, 1KAT) which has been confirmed by conventional techniques [2].

In his monograph [3], the author has suggested the concept of Reaction Analysis, which summarizes techniques and strategies capable of classifying chemical reactions directly. For a homogeneous kinetic model based on r steps, he considered a formulation for the time-dependence of an appropriate physical quantity of measurement, $x(t)$, and its derivative, $y(t)$, aimed at separation of kinetic from substance-related information

$$y(t) = \frac{dx}{dt} = \sum_{i=1}^{r} \frac{dx_i}{dt} = \sum_{i=1}^{r} \lambda_i \cdot k_i\,[T(t)] \cdot \pi_i(t), \tag{1}$$

where

λ_i = total change of x for the respective method for step i (signal parameter)

k_i = rate coefficient for step i

$T(t)$ = temperature program

$\pi_i(t)$ = temporal concentration (unimolecular step i) or product of two concentrations (bimolecular step i).

This equation is based on the general reaction matrix in homogeneous kinetics (r reactions and s species), characterizing the ODE system [4, 5], involving the stoichiometric coefficients ν_{ij} and leading to the following matrix for the concentration changes of component j,

$${}^{s}_{j=1}\left(\frac{dc_j}{dt} = \sum_{i=1}^{r} -\nu_{ij} \cdot k_i\,[T(t)] \cdot \pi_i(t) \right). \tag{2}$$

Consequently, the kinetic term $\pi_i(t)$ can be expressed using the equation

$$\pi_i(t) = \prod_{j=1}^{s} c_j(t)^{\delta_{ij} \cdot (-\nu_{ij})} \tag{3}$$

if $\delta_{ij} = 1$ for $\nu_{ij} < 0$, $\delta_{ij} = 0$ for $\nu_{ij} >= 0$.

In order to come to general statements, the reaction is followed over the total temperature range accessible, using the Arrhenius Law as an approximation for all particular steps,

$$k_i = k_{i\infty} \exp(-E_i / RT) = k_{i\infty} \exp(-E_i / mRt), \tag{4}$$

For the computer simulation of ca. 2500 kinetic runs due to Eqs (1)–(4), a linear temperature program (heating rate m) was used [3, 6, 7] and, in contrast to the evaluation of our ca. 3200 DTA-experiments, temperature feedback by the reaction heat was neglected.

A further prerequisite was assuming λ_i-values independent of temperature, which is practically realized for many methods of Thermal Analysis (exactly: TG and MS; approximately: DSC, DTA etc.), since the temporal changes of λ_i are usually negligible compared to the paramount changes of the exponential terms in Eq. (4).

The signal parameters λ_i in Eq. (1) represent the static influence of the features of the species in the light of the technique chosen, whereas the products $k_i \cdot \pi_i$ are purely kinetic quantities. With view to the kinetic features of models, the reaction order n, which is in isothermal chemical kinetics the usual quantity for discussion [8], for a non-isothermal approach gains a doublefold signification. Because the heating rate is an additional 'transmitter' parameter, there are now two 'response' quantities, available from an experiment, and for an elementary reaction nearly invariant with respect to the activation data. Both allow to calculate the reaction order, but are based on basically different features of the plot, namely on the asymmetry (shape index S [9, 10]) and on the height (alternatively, halfwidth: Reaction type index M [11–14]; cf. [15–17]).

The meaning of M is based on Semenov's early observation [18, 19] that during an adiabatic gas reaction, reaching of a definite temperature difference (which is given by the activation data) must cause an infinite, explosive self-heating. Therefore, for time-linear guiding of the reaction temperature T, this M represents the reciprocal halfwidth or, alternatively, the peak height, but then standardized with respect to the activation data and the starting concentration(s). M may be calculated via Eqs (5) and (7) from the activation data E and k_∞ and the halfwidth h which corresponds to Semenov's special temperature difference. For a first-order process, we have called the corresponding time 'specific time', u_m [20]. It is available iteratively from heating rate m and activation data, using the approximation

$$u_m = \frac{E}{R\,m\,(\ln k_\infty + \ln u_m)^2}\,. \tag{5}$$

For a one-step process, the mechanistic coordinates S and M depend only on the reaction order n and, for $n \neq 1$, also on the initial concentration c_o of the deficient component:

$$S = \frac{n^2\,(1.25 + 0.21n)}{n^2 + 1.59}\,F_S \tag{6}$$

and

$$M=\frac{R}{\lg^2 e\cdot 2.25\cdot n^{0.52}}F_{\mathrm{M}}=\frac{E}{h\,(\lg k_\infty-\lg\,(uk)_{\mathrm{m}}+\lg u_{\mathrm{m}})^2}\,. \tag{7}$$

For a reaction $n\mathrm{A} \rightarrow$ products and an initial concentration c_o of unity, F_{M} and F_{S} are also unity; for $c_o \neq 1$ and $n \neq 1$, these correction factors are weakly dependent on c_o [10, 14, 21, 22].

For a reaction A+B $\rightarrow$ products, one obtains for the correction

$$F_{\mathrm{M}}=\left(\frac{\lg k_\infty-\lg\,(uk)_{\mathrm{m}}+\lg u_{\mathrm{m}}}{\lg k_\infty+\lg u_{\mathrm{m}}}\right)^2. \tag{8}$$

The product of the specific time with the rate coefficient at the rate maximum, $(uk)_{\mathrm{m}}$, is also an invariant, defined by n (ref). It is unity for $n=1$, but depends on c_o for $n \neq 1$. (TCRC - Theory of Characteristic Rate Coefficients [13]; cf. [16, 17, 23]).

For the characterization of the reaction mechanism of complex processes, the values S (or a similar quantity, e.g. the slope ratio at the half height points) and M are the best of the 15 most easily available parameters [11, 24, 25]. Then, both mechanistic coordinates reveal typical deviations from the invariant expectation values given by Eqs (6) and (7), depending on the type of model and on the activation data of the other reaction steps, compared with that of the reference reaction.

However, the latter dependence contradicts our postulation of parameters which are exclusively model-dependent [26]. Therefore, for any concentration series considered, a 3 X N - matrix was defined, which represents rather behaviour modes than numerical quantities and is termed 'MCC' (Mechanistic Concentration Code). The three lines describe the dependences of the reponse parameters S, Mn(init) and Mn(ov) ($n = 1$ or 2, see later) on c_o (as the transmitter parameter), and the rows enumerate those N intervals of ln c_o, wherein the type of dependence of the response parameter is maintained: increasing(+), decreasing(–) or constant(*C*). For the '*C*'-symbols, a subclassification indicating the corresponding order was introduced [27, 28]. Hence, a '*C*'-type element of this matrix has a double nature; it indicates a rate-determining step, but also represents the order and, hence, gives hints to the stoichiometry and to the position of this step in the total network.

In this article, I report on the influences of the activation and signal parameters on the MCC's of the two-step models. Complementing our experimental material by the results of an extended computer project seemed ambitious, but undispensable: First, the problem of the Reliability of Kinetic Data was recognized as predominant by the ICTA, giving rise to establish an ICTA Kinetics Committee in 1985 [29]. Second, in the study of poorly studied systems with unknown kinetics – the typical sample for the concept of reaction analysis –, closed circuits can often not be assumed so that thermodynamic relationships which would reduce the possible range of signal parameters can scarcely be utilized. Third, even predictions of the activation energies in dependence of signal parameters, based on the Transition State Theory and the reaction enthalpy [30], are so strongly dependent on the type of the transition complex that the reduction of the possibilities to be discussed would be sparse also from this view.

Terminology of the models

The studies were restricted to the homogeneous one- and two-step models. Based on the phenomenology of non-isothermal reaction signals, the following very practicable notations are used [31]:

Parallel (= *P*), consecutive (= *F*), opposing (= *G*) and independent (= *U*) reactions.

The molecularities of the steps shall occupy the subsequent places in the abbreviations, 1 for an unimolecular, 2 (or AB) for a bimolecular step with equal (or different) initial concentrations of the reactants, e.g.

$$\mathrm{F1AB: A \rightarrow X \xrightarrow{+B} END.}$$

For one reaction and molecularities < 3, apart from the cases 1, 2 and AB from above, two special types occur: 2A = reaction A+B → B+B (bimolecular autocatalysis) and 1KAT = reaction A+K → B+K (catalysis). In this study, 25 two-step models [27] are considered. The first index shall define the reference reaction, which is, logically, the first reaction for the F- and G-types, but, temporally, the first reaction for the P- and U-types, since then it occurs at the lower temperature.

For feedback mechanisms, the next place is reserved for '*T*' which signifies a reaction between reactant and transient,

$$\mathrm{PABT: A \xrightarrow{+B} X \xrightarrow{+A} END.}$$

It is worth mentioning that in heterogeneous kinetics rather geometrically founded mechanisms have been summarized, but mostly restricted to one kinetically effective process [32].

Details of computation

All computations were performed using the VAX/VMS-system of DEC. The heating rate was m= 1.5 deg/min., which is in a range of approximate redundance for an equipment for reactions in stirred solution.

Simulation of series of signals

The non-isothermal signals due to Eqs (1)–(4) were generated by numerical integration, using a program as one component of an intelligent program package developed for theory and practice of non-isothermal reaction kinetics since 1970 [1, 33–35]. This contains programs for evaluation, graphic representation, and data banks, and was complemented by an improved Gear subroutine [12, 36]. The latter was successfully applied to very complex, even oscillatory models [28, 37]. The usually bell-shaped derivative signals in practice do not start at absolute zero, but at a temperature which can be precalculated for a one-step process, based on the TCRC, corresponding to ca. 85% of T_m, the absolute temperature at the rate maximum of a first-order reaction (for a heating rate 0.5–5 deg/min and a threshold at onset of 0.05–0.5% of the amplitude). Such signals end at 110–145% of T_m, but especially this final temperature is highly dependent on the reaction order. The TCRC only admits rough precalculations of the initial and final temperatures and times, whilst for a complex process the final temperature is rather unknown before the integration. The author has developed additional approximations for the start and final times of different model types, completed by a repetitive regulating algorithm aimed at searching start and end point of the curves (cf. "Fuzzy-Technology).

The generation of curves under variation of c_o (from $5\cdot10^{-3}$ to 10^{+2} M) was performed automatically; after the last numerical integration, recognized as satisfactory, the plot was submitted to an evaluation algorithm (see later), and the difference of the S or M value compared to the previous course was used for precalculating an adequate c_o for the next curve. Since in concentration ranges with a strong value density the number of courses was increased, the program even allows a careful study of small, critical concentration ranges, e.g. near to an instability point. In general, 30–40 c_o-valves, i.e. curves are sufficient to reflect the peculiarities of any two-step model.

Determination of the mechanistic coordinates

Under assumption of a one-step reference reaction and referring the total conversion to unit reactant concentration, the rate coefficients at 100–150 equidistant points of the $y(t)$-Kurve were determined. Then, four sets of activation data were taken over from the Arrhenius fit: alternatively, first- or second-order, and either the initial (25%) or overall time range were assumed [25, 34]. Finally, S and M were determined under exclusion of such two-peak records where the minimum was below the half maximum of the last, splitted part.

Both the signal generation and evaluation procedures were checked by various chemical reactions with activation data determined by conventional techniques.

The MCC's and their determination from a series

The code strings are formed by the following procedure for the 15–49 points (belonging to one plot each) of the serial $M(c_o)$- and $S(c_o)$-functions: considering two neighbouring points for increasing reactant concentration, the new symbol is derived from the position of the next point compared with the vertical tolerance interval fixed by the previous point. If the new value of the response parameter is inside, the element is '*C*' (constancy): otherwise, '+' or '–'. If the next point yields a different symbol, a new interval is opened whereas in the opposite case the interval is expanded. Starting from c_{min}, this iterative instruction is continued until c_{max} has been reached. Intermediate cases are determined by comparing the slope of an approximate straight line in the closed interval, leading to elements as '*C*)' or '+').

The procedure was applied both manually, and by a computer program based on a given tolerance. For generating the total set of intervals, the common set of all limits of the three MCC strings was used in order to store all kinetic peculiarities of the two-step model, which usually leads to 4–10 intervals.

The signification of the symbols '*C*'s '+' and '–' was recently refined [1, 27, 28]. For the mechanististic coordinates, the '*C*' was replaced by order-indicating symbols $L(n<1)$, 1, M $(1<n<2)$, 2 and H $(n>2)$. Further, a second symbol may be added for any element, creating mixed symbols (*L*–, *M*+ etc. = nearly constant but small decrease or increase; –*m*, +*h*, +1 etc. = moderate decrease or increase in region *M* , *H*, 1, etc.). For true constancy (*L*, 1, *M* etc.), the second space may be used to indicate intermediate regions (L1, 2h, 1m etc.). The decision between cases such as '*C*+' and '*C*' is reached by fixed barriers for the slopes of the straight lines fitted in the respective intervals. This terminology has the advantage that the first symbol remains as the predominant, so that for a simplified view the second symbol may be omitted.

For special instabilities (extreme increase or decrease), the symbols '/', '\', '↑' and '↓' are proposed for the second space where e.g. '↑' means an extreme increase to a sharp peak, followed discontinuously by a steep decrease. This situation holds e.g. in mechanisms with AB steps at the 1:1 reactant barrier.

Influence of the activation data and signal parameters

General

Due to the mode of their construction, the MCC's usually reveal only a minor dependence on the activation data; therefore, only certain E_1/E_2- and λ_1/λ_2-pairs were considered. On the other hand, the sign of the difference E_2-E_1 causes two different strings for many models (as had been expected e.g. for opposing reactions: endothermal DTA signals show one peak, but exothermal two peaks of inverse sign). Thus, we mostly distinguished the following cases of E_1, E_2 (cf. Table 1): a) normal, 15 and 20 kcal/mol, b) normal/inverse, 15 and 10 (index *), c) equal, 15 and 15. d) narrow, 15 and 17. e) parallel, 7.5 and 10. f) wide, 10 and 22. g) extremely wide, 3 and 15. h) slow, 15 and 20, but log $k_{1\infty} = 9$ (referred to min) instead of usually 12. i) fast, 15 and 20, but log $k_{1\infty} = 15$; further, the inverse *-type was also studied for the narrow and wide difference of the activation energies.

One characteristic feature of a concentration-based code string compared with another, fixed string, is a shift, which appears if one activation parameter and, hence, the rate is changed so that the first or last element may disappear for a given concentration range. Hence, for the creation of complete MCC's it was important that both reactions undergo a real interference, which is maximum in the centre of this range. Therefore, after selection of both activation parameters and the first frequency factor, the second was adjusted for preferentially $c_0 = 0.2$ in a manner that the rates of both steps were equal at the curve maximum (= peak).

With respect to the signal parameters, discussed as relative parameters ($q = \lambda_2/\lambda_1$), the numbers of series were restricted to three cases for each of the 52 two-step models, namely, $q = 1$ (equal weight of both processes), $q = 0.30$ (small contribution of the second reaction) and $q = 3.0$ (small contribution of the first reaction). For the key models, the limiting cases of $q \rightarrow 0$ (second reaction not directly observable), $q \rightarrow \infty$ (first reaction not directly observable), and negative q's were also studied.

MCC's for the special model P12

Table 1 shows the MCC's for different series of the key model P12 (Parallel reactions of first and second order). The results are:

1) For the normal, parallel and narrow cases of the activation data, the three strings are practically equal. The first and the last elements are constant. Excepting the M_1-string ($M_{(ov)}$, $n_{(ref)} = 1$) which reveals a change of n from 1.0 to 1.2, the orders remain the same.

2) For the wide case, the last element may be absent in the M_{10}-string ($M_{(init)}$, $n_{(ref)} = 1$)

3) Change of $k_{1\infty}$ between 10^9 and 10^{12} and a corresponding parallel change of $k_{2\infty}$ has no influence on the MCC.

4) For $q < 0$ ($q = -0.3$), the last element is '+' in both M-strings.

In conclusion, the model P12 is satisfactorily characterised by an invariant code, if negative q-values (which are often irreal) or extreme differences between both activation energies are excluded. Neither the ratio E_1/log $k_{1\infty}$ nor the difference E_2-E_1 or the relative signal parameter shows a distinct influence.

Table 1 Code strings for the model P12 using different activation data and signal pararameters

E_2-E_1 key word	E_1	$\log k_{1\infty}$	E_2	$\log k_{2\infty}$	λ_{rel}	S-string				M0-string				M1-string				
normal	15	12	20	17.01	-0.15	1	+)	1M	+)	1	-)		+	1	-)			+
				17.00	0	1M	+		H)		-	H2	H)	1	+			-)
				17.00	0.30	1	+		2	1	-		2M	1	-	M)	+	1)
				17.00	0.75	1	+		2M	1	-		2M	1	-)	M1	+	1
				17.09	1.00	1	+		2)	1	-		2M	1	-)	M1	+)	1
				17.00	1.30	1	+		M1	1	-		2M	1	M)			1
				17.09	3.00	1	+		2M	1	-		2M	1	-)	M1	+)	1
				17.00	∞	1	+		H	1	-		H	1	-	M	+	1
parallel	7.5	12	10	17.00	0	1	+		H)	1	-		H2	1	-)	M)	+	1)
				16.50	0.75	1	+		2M	1	-		2M	1M	-)		+	1)
				16.92	1.50	1	+		2)	1	-		2)	1	-)	M)		1)
				17.00	∞	1	+		2)	M	-		2	1M	-)	M1		1)
equal	15	12	15.0	12.54	0.30	1	+	-	i	1	-	+)	2M	1	-)	M)	+	L1
				12.54	1.00	1	+		2)	1	-		2M	1	-)	M)	+)	1
				12.40	∞	1	+		2	1M	-		2M	1	-)	M1	+)	1
narrow	15	12	15.5	13.14	1.00	1	+		2M	1	-		2M	1	-)	M	+	1
			17.0	12.16	0.75	1	+		2	1	-		2M	1	-	M)	+	1)
				12.92	1.50	1	+		2	1	-		2M	1	-)	M1	+)	1)
wide	10	8	22	20.50	0	1	+		2M	1	1		1	1	+			L)
				20.50	0.15	1	+		2	1	+	L)	-	1	+)	L)	-	1
				20.50	0.75	1	+		2M	1	+		-	1	+)	L)	-	1
				20.50	1.50	1	+		2M	1L	+	L)	-	1L	+	L)	-	1
				20.50	∞	1M	+		2M		-		2M				-	1)
	15		25	21.20	0.75	1	+	M)	2	1	-		2	1	1M			1
extremely wide	3	6	15	33.05	1.50	1	-	+	2	1	+		L)	1	+			-
				32.15	∞		+	M)	+) M2		+	-	2		+	L)	-	M1
slow	15	9	20	13.13	0.30	1	+	H)	2	1	-		2M	1	-)	M)	+)	1
				13.13	1.00	1	+		2M	1	-		2M	1	-	M1	+)	1
				13.16	3.00	1	+		2)	1	-		2M	1	-)	M1	-)	1)
fast	15	15	20	21.00	0.30	1)	+		2M	1	-		2M	1	-)	M)	-)	M+1
				22.00	1.00	1	+		2M	1	-		2M	1	-)	M)	+)	1)
				21.07	3.00	1	+		M)	1	-		2	1	-)	M)	+)	M)

Activation data: referred to kcal/mole (E), min^{-1} or $\text{dm}^3\ \text{mole}^{-1}\ \text{min}^{-1}$ (k_∞)
A-factor $k_{2\infty}$: optimized for optimal interference (see text)
Codes in simplified terminology: 2) means possibly not constant, +) possibly constant etc.

Influence of the activation parameters in other models

The general shift of a code string *vs.* a fixed string, caused by a change of one activation parameter, cannot act linearly over the total concentration range. Especially for intervals representative of small slopes of one of the three mechanistic coordinates, a restriction or extension of the string by appearing or vanishing intervals of indistinct constancy (M+, H) etc.) cannot be excluded.

Due to the concept applied, the influence of the activation energies on the codes should be negligible as for the P12-model. Variations occur especially for the wide cases where also new 'C'- or 'C)'- intervals inside (which are often pretended by a maximum or minimum) may appear. Nevertheless extremely high differences E_2-E_1, depending on the model, can cause a degeneration of a string. Such a degeneration becomes predominant in parallel or independent types composed of two second-order steps (P22 and U22) where in the narrow or equal case only a single second-order process (type 2) is indicated.

The direct influence of the rate (realized by varying the first A-factor, $k_{1\infty}$; slow and fast case) on the code is even smaller than that of the activation energies: if $\lg k_m << \lg k_\infty$ in Eq. (7), the shifts must reveal a rather linear correlation of $\ln(c_o)$ to $\ln(k_{1\infty})$.

Structure of the MCC-strings and influence of the signal parameters

Because of the surprisingly small influence also of the signal parameters, the three code strings were dissected into main parts, remaining invariant, and residual parts, expressing a dependence on the signal parameter q. The general architecture is the same for all models: The first element signals constancy for infinitely small c_o and mostly corresponds to the order of the reference process; the last element (for high c_o) behaves similarly; however, the corresponding order may differ from that of the reference process even more (Table 2). Both reaction orders may be changed or may even be fractional for the special situations in some models. For the M-strings, such effects are caused by the c_o-dependent term $(uk)_m$ in the denominator of Eq. (7), used for a correction of M [13, 14, 27]. For some – mostly consecutive – mechanisms, stationarities cannot really be reached for both limiting elements (e.g. P2A*, F12(*), F22); sufficient suppression of one of the steps fails then.

As invariant main elements inside the string, there are 0–4 '+' or '–' elements for S, 0–2 for $M_{(init)}$ (even 3 for models F21*, FAB2, U2AB) and similarly for $M_{(ov)}$ (even 3 for models P1AB, F21*, FAB2, U2AB; Table 3; the limiting elements are omitted). It is instructive to compare the succession of the signs with those in the simple AB-reaction. The remaining influence of q on the residual strings of the complete MCC's as shown in Table 3 (cases q = low, unity, high) is relatively small. By the use of an adequate rating system, taking 1 for total agreement of two double symbols, 0 for total disagreement, 0.5 for partial agreement (e.g. 'M)' *vs.* 'M') and 0.75 for overwhelming agreement (two 'C'-type elements, but different orders) it can be shown that the minimal rating (assuming the strongest scatter caused by the q-variations) means at least 94% probability for the P-models, 84% for the F-models and 80% for the U-models, when the limiting

Table 2 First and last elements for the MCC's of all one- and two-step models

Model	First element			Last element		
	S	MØ	M	S	MØ	M
– One step –						
1	1	1	1	(is the first)		
AB$^{1)}$	1	1	1	1	M	1
2	2	2	2	(is the first)		
3	H	–)	–)	H	H	L
1B$^{2)}$	M	1	1	1	1	1
– Two steps, competitive –						
P12	1	1	1	$2M^{h)}$	2M	$M1^{=)}$
P12*	1	1	1	$2^{h)}$	2M	$1L^{*)}$
P21	1	1	$2M^{l)}$	$2M^{=)}$	2M	2
P21*	$1M^{l)}$	1	$1M^{=)}$	$2^{h)}$	2M	$2M^{l)}$
P22	2M	2M	2	2M	2M	2
P1T	1	1	~1	1	$2M^{*)}$	$M^{l)}$
P1T*	$1^{l)}$	1	1	$1^{l)}$	$1^{*)}$	$1^{h)}$
P2T	2	–)$^{*)}$	$2H^{*)}$	M	$-^{=)}$	$H^{h)}$
P1AB$^{1)}$	1	1	1	1	$+^{*)}$	$1^{-h)}$
P1AB*	1	$L^{*)}$	$L1^{*)}$	1	$L^{-*)}$	$L^{-l)}$
P2AB	1	$1^{h)}$	1	2	$2M^{h)}$	$1M^{*)}$
P2AB*	1	1	1	$2^{h)}$	$M2^{h)}$	$1M^{l)}$
PAB1	$1^{h)}$	$1^{l)}$	1	$\uparrow^{=)}$	$\uparrow^{*)}$	$L^{*)}$
PAB1*	1	$L^{l)}$	1L	$L^{*)}$	$1^{l)}$	$1^{h)}$
PAB2	1	1	1	$2M^{*)}$	2M	M1
PAB2*	1	1	1	2	$M2^{*)}$	$1^{*)}$
PABT	1	1	1	$L1^{*)}$	$L^{*)}$	$L^{*)}$
PBA1$^{3)}$	$1^{h)}$	$1^{l)}$	$M1^{h)}$	1	$1^{h)}$	$1^{h)}$
PBA2$^{3)}$	2M	2M	$1^{1)}$	$1^{h)}$	$1^{*)}$	$M1^{*)}$
PBA1*	1	L1	$1M^{*)}$	1	1	1
PBA2*	2	$M^{l)}$	$1^{h)}$	1	$1^{h)}$	1

Model	First element			Last element		
	S	MØ	M	S	MØ	M
– Two steps, consecutive –						
F12	$-^{*)}$	$H^{+=)}$	$M^{-=)}$	1	$-^{*)}$	$M^{*)}$
F12*	$M^{*)}$	$1^{*)}$	$-^{h)}$	1	$M^{h)}$	$M1^{l)}$
F21	2	$2M^{h)}$	2	$+^{*)}$	$-^{=)}$	$H^{=)}$
F21*	$1^{=)}$	$2^{l)}$	2	$1^{l)}$	$M2^{*)}$	$+^{*)}$
F22	–	$M^{-*)}$	$M^{*)}$	$M^{+*)}$	$H^{-*)}$	$H^{*)}$
F22*	$+^{*)}$	$-^{h)}$	$-^{h)}$	$2^{l)}$	$2M^{*)}$	2
F1AB$^{1)}$	$1^{l)}$	$M^{l)}$	$2^{*)}$	1	1	1
F1AB*	$+^{*)}$	$H^{*)}$	$M^{=)}$	1	1	1
F2AB	2	$2^{-*)}$	$1^{l)}$	2	2M	1
F2AB*	$2^{h)}$	$2M^{h)}$	$M2^{=)}$	$2^{l)}$	2M	1
FAB1	$1^{l)}$	$L^{l)}$	$L^{=)}$	$-^{l)}$	$-^{l)}$	$L^{l)}$
FAB1*	$M1^{l)}$	$M^{h)}$	1	$+^{=)}$	$H^{*)}$	$M2^{=)}$
FAB2	$-^{1*)}$	$H^{+*)}$	$-^{l)}$	$H^{-*)}$	$H^{*)}$	+
FAB2*	$M^{*)}$	$L^{*)}$	–	$M^{l)}$	$-^{=)}$	$L^{*)}$
– Two steps, independent –						
U12	2M	$2^{h)}$	1	1	1	1
U12*	2	$2M^{l)}$	$1M^{l)}$	1	$1^{-l)}$	$1^{-h)}$
U21	1	1	1	2	$2M^{*)}$	$1^{l)}$
U21*	1	1	1	2	2M	$1^{h)}$
U22	2	2	$1^{h)}$	$2^{h)}$	2M	$1^{*)}$
U1AB$^{1)}$	2	$2^{l)}$	1	$1^{h)}$	1	$1^{h)}$
U1AB*	2	2M	$L^{h)}$	1	$L1^{h)}$	1
U2AB	$2M^{=)}$	2M	$1^{l)}$	$2^{l)}$	2M	1
U2AB*	2	2M	$1^{=)}$	$2^{h)}$	2M	$1^{*)}$
UAB1	1	1	1	$1L^{*)}$	$-^{=)}$	+
UAB1*	1	1	1	$M^{-*)}$	$1^{h)}$	$+^{h)}$
UAB2	$2^{h)}$	$2M^{*)}$	1	$H^{+*)}$	$-^{l)}$	$M2^{*)}$
UAB2*	2	$M2^{*)}$	$L^{l)}$	$-^{*)}$	$1L^{h)}$	$+^{h)}$

A_o is varied; Changes mostly refer to the specifications of the 'C'-quality, especially for the P- and U-models.

l) Change for low λ's; $^{h)}$ Change for high λ's; $^{*)}$ Change for low and high λ's; $^{=)}$ Equal Change for small and high λ's

1) B_o=1, A_o is varied; 2) Reactions A+B →2B+Prod; B_o is varied; 3) As reactions PAB1 and PAB2; but B_o is varied

elements are included. This means that the MCC indeed allows a direct determination of models from experiments since >80% of the elements agree with the standard model elements, and this value is increased after separate evaluation of several-peaks records and, further, by the involvement of the opposing G-models where $q_1 = q_2$ can be assumed.

By logical inversion of Table 3, taking the first two or three main elements as the vehicle for the classification, a – not always unambiguous – assignment of the optimum model becomes possible. Then, together with the logistics of the orders

Table 3 Internal parts of the MCC-strings for several basic models and their dependences on the signal parameters

Model	S-string	M(init)-string	M(ov)-string
AB	⊕ ⊖	⊖ ⊕	⊖ ⊕
P12	0 0 0 ⊕ 0 0 0	0 0 0 ⊖ 0 0 0	0 M1 0 ⊖ 1M+ 0 M
P12*	0 0 0 0 ⊕ 2^- ⊖ 0 0 0 0	0 0 + L1 ⊕ 0 ⊖ 0 0 0 L)	0 0 – 0 ⊖ M ⊕ 0 +1L 0 0
P21	0 0 0 ⊕ –) 0 ↑–	0 0 0 ⊖ H)+ 0 0	0 2 2^+ 0 ⊖ 2H ⊕ 0 0 H 2^-
P22	2)+2+) 0 –)?	–) 0 +)–)	–) 0 +)–)
P1T	0 1M 0 – ⊕ 0 ⊖ 0 0 0 0	–) 0 0 0 ⊕ 0 ⊖ 0 0 L) 0	0 e) 0 0 0 ⊕ 0 ⊖ 0 0 0 0
P1T*	0 1M 0 0 ⊕ 0 ⊖ 0 0 0 0	+)L) 0 –)? ⊕ 0 0 0	0 e) M1 e) 0 0 ⊖ M) ⊕ 0 0 M 0
P2T	0 e) 0 0 0 ⊕ H) ⊖ +) – 0 M)+M	0 M 0 –)2H ⊕ 1 ⊖ 0 0 0 0	0 M2 h) 0 0 ⊕ M) ⊖ 0 –H2 0 0
P1AB	0 ↑ + 0 ⊕ ↑ ⊖ ↓+ 0 M+↓ 0	0 0 h) 0 0 ⊖ M ⊕ –H 0 0 ↓–H+2)	0 +L– 0 e) 0 ⊖ M) ⊖ 2 ⊕ 0 +↓ 2)
P1AB*	0 0 0 0 ⊖ 0 ⊕ 0 0 ↓ 0	0 – 0 ⊕ 0 1–M+ 0	0 0 h) 0 0 ⊕ L^- ⊖ 0 0 L^+ 0

Table 3 Continued

Model	S-string	M(init)-string	M(ov)-string
P2AB*	0 M 0 0 ⊕ M^+ ⊕ 0 0 M^+ 0	0 0 0 1 ⊖ M^- ⊖ 0 −M M^+ 0	0 ↓ 0 0 ⊖ ↓ ⊕ 0 0 ↓ 0
PAB1	1^- 0 1 ⊕ ↑− 1L L)	− 0 1 ⊕ ↑− +)1 0	0 ↓ 1M+ 0 ⊖ ↓ ⊕ − 0 ↓ 1L
F12	0 0 0 0 0 ⊖ 0 ⊕ M ⊖ 0 0 ↑ M 0	−M) 0 0 0 ⊕ L^+ ⊖ 0 ↑ 0 0	0 0 0 0 ⊖ 0 ⊕ 0 0 2H) -)L)-1)
F21	0 0 0 − 0 ⊕ 0 ⊖ 0 ⊕ +1 0 0 0 0	0 0 0 0 ⊖ 0 ⊕ 0 0 2H) -)L)-1)	0 2M) h) M)+ 0 ⊕ 0 ⊖ 0 0 0 0
F21*	0 0 ↑ 0 0 ⊖ 0 ⊕ ↑ ⊖ 0 +) 0 l)+) +	0 l) 0 0 0 0 ⊕ M^- ⊖ H ⊕ 0 0 M) 0 0	0 l) 0 2H 0 2^+ ⊕ 0 ⊖ L ⊕ 0 0 2M 0 0
F22	0 M) h) 0 0 ⊖ 1 ⊕ 0 2M 0 0	0 0 0 ⊖ 0 0 L)-)	0 h) 0 0 ⊖ 0 0 +)
F1AB	0 l) M^- 0 +)1 ⊕ 0 ⊖ 0 − 0 +)	0 l) 0 0 0 ⊖ H ⊕ 0 0 H) 0	0 ↑ 0 0 ⊕ M)+ ⊖ 0 0 0 +
FAB1	0 ↑ 0 0 ↑ 0 ⊕ ↑ ⊖ L1 ⊕ 0 ⊖ 0 0 ↑ l 0 0	0 ↓ l)− 0 0 ⊖ L^- ⊕ 0 0 ↑ L+↑	0 ↓ M 0 ⊖ ↓ ⊕ 1+ 0 ↓ 0
FAB2	0 − ↑ 0 ↑− 0 ⊕ 1 ⊕ H ⊖ l) ⊕ 0 − M2 ↑ M2−↑ 0	0 0 ↓ M+ 0 ⊕ 0 ⊖ 1 ⊕ −L− M^- 0 ↑ −+	0 0 0 M+ 0 ⊕ L) ⊖ ↓ ⊕ L)-2M 0 L^- ↓) 1^-
U12*	0 0 0 ⊖ +) 0 L)	0 0 0 0 ⊕ 0 ⊖ 0 0 L^- 0	0 0 0 0 ⊕ ↑ ⊖ 0 0 0 0
U2AB	0 h) 0 2^+ 2^- l) 2^+ 0 0 ⊕ 0 ⊖ 0 ⊕ 0 ⊖ 0 0 2^- 0 0 0	− 0 2^+ 0 2^- ⊕ 0 ⊖ 2^+ ⊕ 0 0 0 0 0	0 h) 0 ↓ 0 0 ⊕ 0 ⊖ ↓ ⊕ M+ 0 0 0 M−+

Vertical rows: First element $\lambda = 0.3$
(Residual strings) Second element $\lambda = 1.0$
Third element $\lambda = 3.0$

$\begin{pmatrix}0\\0\\0\end{pmatrix}$ means: independent of λ

Sign symbols + and −: These disappear, if marked by l), n) or h), at low, normal or high λ, -respectively.

in the limiting elements (Table 2), also an unambiguous model determination should be reached.

Concluding remarks

The postulated 'Theorem of Common Kinetic Runs' is not strictly valid, but a useful approximate concept, readily applicable to the elucidation of reactions in solution, if in signals with nearly isolated maxima each peak is treated separately.

The three symbol strings form the MCC, a parameter set of optimum kinetic reliability, which, basically, involves only two dimensions of information: the two proposed M-parameters represent alternatives, but their common use seems well-founded because a ready comparison with usual kinetic procedures is possible, as are the initial rate methods and the estimation of overall data, a widespread, although often misleading practice.

The one-step strategy for the evaluaton was established in order to study an optimistic, simple expectation, and then to draw exact conclusions from the deviations, using a recursive concept. One problem in gaining reliable overall data is the use of an appropriate weighting procedure [34, 38], but such unavoidable shortcomings are partially compensated for by the application of the same evaluation program to both experimental and theoretical records. This concept raises the rather materialistic level of the well-proven reference techniques, realized by twin arrangements [6, 39], to the rather intellectual level of reference-based evaluation strategies [27, 40]. Experience in the application of probability theory [1, 41] will facilitate a realiable interpretation of the thermoanalytical patterns obtained.

The first extensive study of our experimental DTA plots using both the MCC-concept [1] and self-constructed equipment for stirred homogeneous solutions [3, 39, 42, 43], and the study of kinetic UV plots [44] are now complemented by this global study of the signal parameters, which is required in order to fully utilize multiple techniques. With view to more complex reactions, where the first test using MCC's was recently published [28], the path of characterizing a reacting system exclusively with respect to its kinetics should allow a separation of redundant, nonkinetic data by a concise classification and archivation of those processes which can be studied in real-time, regardless of the method used and the (static) features of the components. Considering the success in also recognizing three- and four-step models by assuming superpositions of two two-step models [1], we will probably learn to translate rather complex MCC's to the readily interpretable reaction matrices in the near future.

Also in isothermal kinetics, where the role of the shape index is rather questionable and only one type of string, that related to the halfwidth, is easily interpretable, the proposed way should enhance the effectivity of interpretation; but non-isothermal kinetics studies represent a more general approach to kinetics because they include temperature as a general parameter of information. The advantages of such analyses in solution became obvious in studies of intermediates at low temperatures [11, 45, 46].

For the solid phase, the interpretation of kinetic studies (which are also very useful for the development of High-Tech components [6, 47, 48]) is much more difficult because of the influence of both transport processes and feedback effects of reactants moved into another phase [49]. An improvement of the usual kinetic strategies [12, 50, 51] could probably be reached using similar concepts based on standardized kinetic patterns, but using the heating rate or other transmitter parameters. However, this will be impossible without a global and appropriate classification concept for several superposed chemical and/or physical processes. Further, commercial equipment can only meet with the aim of determining models if reliable calibration procedures, desirably forwarded by the manufacturers, have been developed.

* * *

The continuous interest and the stimulating ideas of Prof. Dr. O. E. Polansky over the twenty years of our collaboration and the subsequent generous support of this work by Prof. Dr. D. Schulte-Frohlinde are gratefully acknowledged. Apart from the assistance of many coworkers, appreciated in the respective articles, I am very obliged to Prof. Dr. R. J. Field for his suggestions for the numerical integrations and having sent a Gear subroutine; to Prof. Dr. E. Körös for his proposals concerning the analytical techniques; and to W. Angenendt, Dr. B. Weimann and Prof. Dr. E. Ziegler of the joint computer department of both Max-Planck-Institutes in Mülheim for stimulating discussions and help in programming.

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Zusammenfassung — Die kinetischen Eigenschaften der homogenen Zweistufen-Modelle wurden durch die Auswertung von 2500 Kurven systematisch untersucht, die durch Computersimulationen für linear ansteigende Temperatur erhalten und mit zahlreichen Experimenten verglichen wurden. Für Methoden, bei denen jede Teilrate zu ihrem Beitrag zum derivativen Gesamtsignal proportional ist, wurde gefunden, daß aus der Halbwertsbreite und dem Formfaktor der Kurven verhaltenstypische Sätze dreier, von der Reaktionsordnung abhängiger Parameter ermittelt werden können, die bestimmten Intervallen der Startkonzentration zugeordnet

sind. Solche thermoanalytischen Muster stimmen mit denen, die aus den Verteilungslisten einiger Tausend DTA- und UV-Experimente erhalten wurden, überein und werden für die 21 wichtigsten Zweistufen-Modelle aufgeführt. Sie sind praktisch unabhängig von den Aktivierungsdaten und den methodenspezifischen Proportionalitätsfaktoren; deshalb erlauben sie die direkte Identifizierung des Reaktionsmodells.