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THEORY

WHAT TYPES OF REACTIONS IN SOLUTION REVEAL A RELIABLE ARRHENIUS LINE?

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The interrelations between the correlation coefficients (= r) for an Arrhenius representation (linearity $\ln k$ *vs.* $1/T$) of runs evaluated by the one-step strategy, and their locations in the mechanistic diagram (reaction type index M *vs.* shape index S) are studied, based on 3000 DTA and UV experiments and 850 theoretical curves for 40 reaction mechanisms. It turns out that files corresponding to the source points of first- or second-order, or to the A-region located between, reveal a reliable Arrhenius line; but for particular mechanisms, files attributable to regions rather "distant" from this center, may also behave so. Therefore, further studies must lead to powerful r,S,M-based kinetic pattern recognition methods.

A fundamental kinetic problem in thermal analysis is the following: A reliable straight line (= AL), in the Arrhenius plot $\ln k$ *vs.* $1/T$ was obtained. What, if any, conclusion on a reaction mechanism can then be drawn?

In our data bank, files of 2713 DTA and 279 UV experiments are stored, which represent peroxide and ozonide formation and decomposition reactions, Diels-Alder reactions, diverse unimolecular decompositions or isomerizations, redox reactions of multivalent metal salts, oscillating reactions and various other reactions in solution. A theoretical library contains 847 simulations of rate curves of two-step models and 24 more complicated mechanisms. All files involve various result parameters, such as the readily available mechanistic coordinates S and M (shape index and initial or overall-referred reaction type index [1, 2] and the four correlation coefficients of the fitted AL's for an assumed initial or overall, first- or second-order process.

This static study is applied to an assumed bimolecular reference reaction ($A+B \rightarrow$ products) and restricted to the respective files showing constant heating rate (1.5 deg/min; UV 1.5 or 0.8 deg/min) and adequate signal height (0.2–12K in DTA). For a refined classification of the kinetics, the mechanistic diagram [1, 2] was divided into 5X5 = 25 regions (abbreviations Fig. 1), using the boundary values

S: $0 - 0.5 - 0.63 - 1 - 1.2 - \infty$ and
M: $0 - 0.0121 - 0.01435 - 0.01875 - 0.02205 - \infty$ (kJ/mol K).

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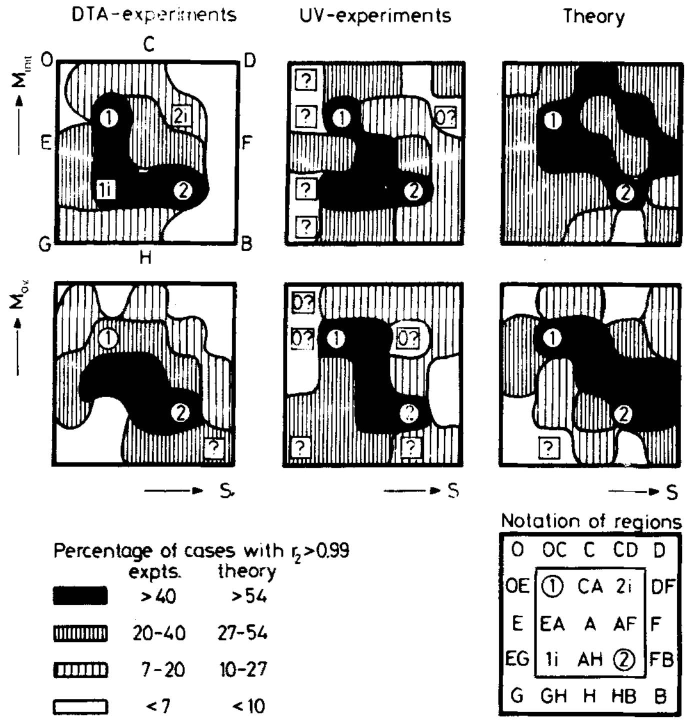


Fig. 1 Distribution of cases with satisfactory Arrhenius straight lines on the 25 regions of the mechanistic diagram (DTA; $r_2 > 0.99$; UV: $r_2 > 0.98$)

First, the distribution of all such files over these 25 regions was studied. Table 1 gives a rough survey.

Table 1 Complexity of experiments and simulations

M-value	Subject	Files AB-type*	 complex
Initial	DTA experiments	250 (28%)	653 (72%)
	UV experiments	40 (17%)	193 (83%)
	frequent regions	1i, EA, A, H	
	rare regions	CD, D, DF, F, FB, B	
	theoretical files	484 (58%)	358 (42%)
Overall	DTA experiments	352 (35%)	653 (65%)
	UV experiment	66 (28%)	166 (72%)
	frequent regions	0E, 1i, CA, EA, E, A	
	rare regions	0C, CD, D, DF, F, FB, B, G, GH, H, HB	
	theoretical files	358 (58%)	256 (42%)

* Region *A* or regions appended to *A*; here, elementary bimolecular processes are located (cf. Fig. 1).

Arrhenius line and mechanistic diagram

Experiments attributable to the 1-area ($A_o \ll B_o$), 2-area ($A_o = B_o$) or A-area ($A_o \neq B_o$) should render a good AL since $k(T)$ was calculated from the bimolecular rate law. In such cases, also the correlation coefficient, r_2, for linearity of ln k *vs.* $1/T$ should be high for each particular experiment. Hence, a key quantity for our discussion is the percentage of cases with $r_2 > 0.99$ (= AL efficiency = ALE); such values are compared for all regions in Fig. 1, using different points of view. In the experimental library, the most cases revealing a satisfactory AL correspond to the regions in the internal square in Fig. 1, including the first- and second-order zones, 1 and 2. However, whilst for an initial diagnosis files corresponding to the elementary regions 1,2 show the highest yield of reliable AL's, for an overall diagnosis this holds for the *A* region. The distribution of the zones according to their ALE's seems to be similar to that observed in the theoretical library, despite of the arbitrary selection of the models investigated. On the other hand, at the right margin of the mechanistic diagram and performing initial statistics in the DTA library, the ALE is small or zero, and the same holds for the regions *G, GH* and *CD, D* and *DF* at the opposite vertices in the overall statistics. This is in contrast to the results with theoretical files, where especially in the initial diagnosis the ALE in cases accumulated at the right margin is quite good. This means that in reality other classes of mechanisms occur than in the model library. Further, the simple two-step models [1] may represent a reliable ALE for certain zones even if these are far away from the central *A* zone, as zones *F, FB, B* or *0E* and *E.*

Arrhenius adaption and a concept of mechanistic distance

Inspite of such obvious exceptions, Figs 1 suggest that there is a correlation between the ALE and the geometric distance of the considered region from the *A*-center. Therefore, in Fig. 2 the ALE, as an average value for all regions of equal distance, is plotted *vs.* this distance, measured in the S–M-plane, and assuming unit distance from one region to the next and equal scales for horizontal and vertical movements. Indeed, the ALE increases if the regions approach to the central region, A.

However, without such an averaging operation, the different regions of equal distance show often extremely varying ALE's. Nevertheless, a satisfactory correlation also for all particular regions can be reached if a more

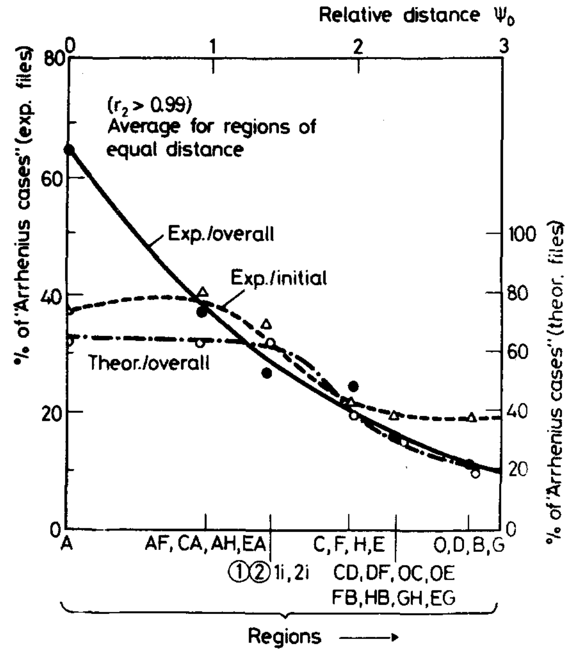


Fig. 2 Metrical distance in the mechanistic plane and Arrhenius cases

complicated distance parameter is defined, namely the geometric mean of the two distances to both the first- and second-order region,

$$\Psi_3 = \sqrt{(d_{s_1}{}^2 + d_{m_1}{}^2)\,(d_{s_2}{}^2 + d_{m_2}{}^2)} \tag{1}$$

wherein the *d*'s represent the corresponding horizontal and vertical distances of the region used. But then the correlation curve is dissected into two branches, see Fig. 3: The upper branch is valid for most of the ALE's of the regions in the triangle with *0–G–B* as vertices whereas the lower branch rather corresponds to the regions of the upper, right triangle *0–D–B*. This means that even this kind of distance does not fix the ALE completely, but the intrusion of the signs of the differences *d* into Eq. 1 leads to an approximate correlation, because these signs determine which branch is valid for this region. The same holds for the overall analysis and for the theoretical data bank (Figs 1, 3) where the ALE's are much higher since experimental fluctuations are absent.

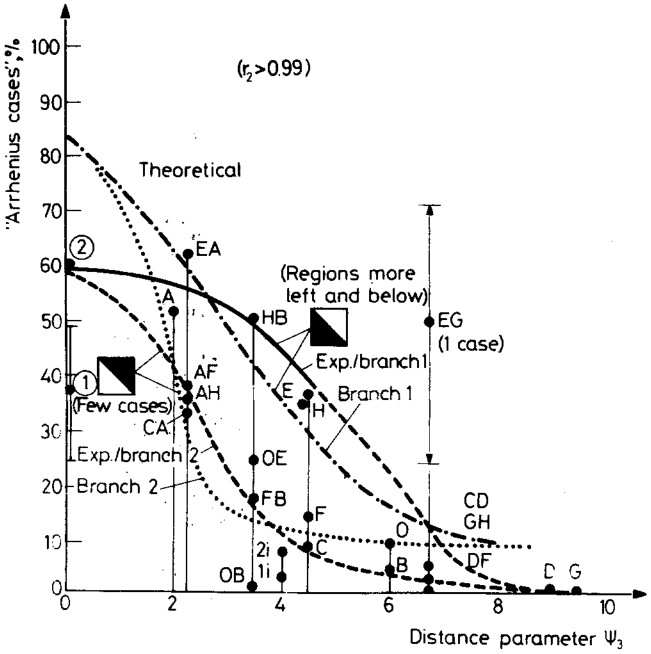
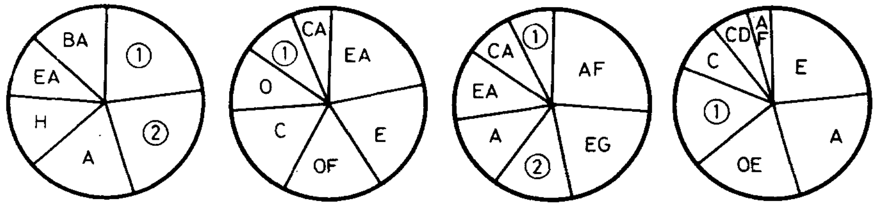


Fig. 3 Correlation branches of the ALE *vs.* distance parameter Ψ_3 for the particular regions (overall statistics)

The usefulness of a distance parameter such as Ψ_3 is caused by the dependence of the mechanistic point S–M of a bimolecular process on the concentration ratio of the reactants, showing the limiting regions 1 and 2 for the pseudo-unimolecular and 1:1 case, respectively.

Distribution for different substance classes and models

The statistically elaborated succession of the regions due to their ALE's should be then independent of the origin of the files (i. e. also of the substance class), if the mechanistic point defines the type of kinetics unambiguously. For rather complex reactions, this is surely not the case in general because the degrees of freedom (2 or 3 per each reaction step) are much more than three ($S+2M$ coordinates). Indeed, the distributions of regions with high ALE's are different for four substance classes investigated (Fig. 4, *overall analysis*). It is true that regions 1, 2 and A describe generally cases with high ALE's (also in the theoretical library). But the succession of these and all other regions with respect to the ALE depends on the substance class.



Simple thermal reactions (oxidations, reductions, Diels-Alder), - 30 % secondary processes of photoreactions

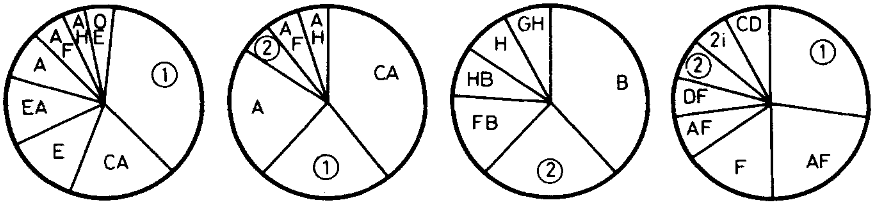
Autocatalytic reactions

Oscillating reactions espec. Belousov-Zhabotinsky reaction

Subsystems of oscillating reactions, e.g. redox reactions with metal ions

Fig. 4 Assorted ALE's for different regions in four sublibraries

Mostly, the regions *CA, AF* and *EA,* which are close to *A*, are the next best candidates. However, in the oscillatory experiments, also region *EG* is strongly preferred, and similarly regions *E, 0E, C* and *0* in experiments involving autocatalysis or subsystems of oscillatory reactions. In contrast, for other types of reactions, such as oxidations, these regions, as also *H, F, D* and *B,* reveal small or zero ALE's.



P_{AB1} A+B → prod. 1
A → prod. 2

P_{AB2} A+B → prod. 1
A+A → prod. 2

P_{2A} A+B → C
A+C → prod.

F_{21} A+A → B
B → prod.

Fig. 5 Essential regions of some two-step models (arranged in the order of increasing ALE)

The approximate theoretical distributions of the appearing regions are presented in Fig. 5 for some two-step models, stemming from 20–25 simulations per model, and based on varied reactant concentration. The paramount differences of these fingerprints ensue from the selectivity of such AL-qualified regions which in the experimental distributions are partially not preferred or even absent. There will be often high ALE's in less frequent regions, e.g. for *B* or *FB* when a special mechanism is present, such as P2A, which differs from the others by its caharacteristic feedback feature.

Outlook

Returning to the position of the chemist who wants to recognize the mechanism really occurring in his experiments, it must be stated that it is difficult to draw conclusions solely from the fact of a good Arrhenius line; the latter is no general indication of an one-step process or, at least, a rate-determining process. Especially in heterogeneous kinetics, it was often stated that the correlation coefficient is a poorly adequate quantity to distinguish between different reaction mechanisms. [4] But this study reveals that a concerted examination of both mechanistic coordinates and the ALE is an appropriate basis for the development of promising pattern recognition methods in homogeneous [5] and possibly also in heterogeneous reaction kinetics.

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Zusammenfassung – Ausgehend von über 3000 DTA- und UV-Experimenten sowie 850 theoretischen Kurven nach 40 verschiedenen Reaktionsmechanismen wird die Wechselbeziehung zwischen den Korrelationskoeffizienten ($\triangleq r$) für eine Arrhenius-Darstellung (Linearität von ln k gegen T^{-1}) und der Lage im mechanistischen Diagramm (Reaktionstypindex M gegen Formidex S) untersucht. Dabei zeigt sich, daß die Diagramme, die den Elementarpunkten für Reaktionen erster oder zweiter Ordnung oder dem mittleren A-Bereich dazwischen entsprechen, eine zuverlässige Arrhenius-Gerade liefern, ebenso aber auch einzelne Mechanismen, deren Kurven weiter entfernten Bereichen im M-S-Diagramm zuzuordnen sind. Deshalb sollten weitere Untersuchungen zu leistungsfähigen kinetischen Auswertungsmethoden auf der Basis von r,S,M-Diagrammen führen.

РЕЗЮМЕ — На основе 3000 экспериментальных ДТА и УФ-данных и 850 теоретических кривых для 40 реакционных механизмов исследованы взаимосвязи между коэффициентами корреляции (r) аррениусовских графиков (линейная зависимость ln k от /1 (T), оцененных одноступенчатым методом и их положения на механических диаграммах в координатах показатель типа реакции M и индекс формы S. Оказалось, что ряды, соответствующие исходным точкам реакций первого или второго порядка или А-области, показывают хорошую аррениусовскую прямую. В случае же особых реакционных механизмов, ряды отнесенные к областям скорее "удаленных" от этого центра, ведут себя аналогично. В связи с этим дальнейшие исследования должны привести к мощным кинетическим методам установления структуры на основе r,S,M — параметров.