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COMPUTER CALCULATION OF THE MECHANISM AND ASSOCIATED KINETIC DATA USING A NON-ISOTHERMAL INTEGRAL METHOD

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The applicability of Šatava's integral method for the kinetic description of non-isothermal heterogeneous processes is first discussed. The method is found insensitive as regards distinction between different types of nucleation-growth models. This disadvantage is countered by using additional criteria, such as the interval of straight-line-fitting, the standard deviation and the value of the preexponential factor. The algorithm for the necessary mathematical operations is explained. A graphical printout in the form of a numerical plot available for any computer is described. The program is tested on different processes. It proves suitable for the preliminary classification of processes and for detection of changes in the reaction mechanism by separate analysis of three consecutive parts of the process.

Data comparatively easily obtained from dynamic thermal measurements have led to a considerable rise in the number of papers dealing with the kinetics of thermally activated processes [1]. The characteristic accumulation of recorded chart strips of otherwise stored data is challenged by the use of computers [1, 2]. The purpose of the present communication is to present and discuss a possible algorithm for kinetic data evaluation, based on our previous experience with computer programming directed to the elucidation of the kinetics and mechanisms of heterogeneous processes [3–6].

Formulation

The mathematical procedure is based on the integral method of kinetic data evaluation [1], employing a most simple kinetic equation to describe the time-temperature behaviour of heterogeneous processes [7]. This assumes direct proportionality [1, 7] between two functions, g (α) and $P(T)$, depending respectively on the instantaneous state of the system (represented here by a single parameter, the fractional conversion α) and on the temperature T (controlled from the surrounding system as a linear function of time, and uniform throughout the system investigated). The main advantage is a simple set of α vs. T input data, with no need for measured or computed derivatives.

The establishment of the function $P(T)$ is mathematically complicated, but is based on the integration of known exponential form of the Arrhenius rate constant [8]. In contrast, the function $g(\alpha)$ is usually not known; its analytical form must be predicted via a hypothesis [1] about the physico-geometrical nature of the process in question.

Approximations to the function $P(T)$ have been developed by making different kinds of expansions, yielding $P(T)$ proportional to (ln T) [9], (T) [10, 11] and (1/T) [12, 13]. It follows that straight lines should be obtained when log $g(\alpha)$, for appropriate $g(\alpha)$, is plotted against ln T, T and/or $1/T$; the slope, tan β, gives the activation energy of the process, E, via the respective relations: (4.657 tan βT_m – 1.986 T_m), (4.567 tan βT_2) and (4.567 tan β – 1.986 T), where T_m is the temperature of the maximum reaction rate and T is the mean temperature of the process. Since the determination of activation energies utilizes the slope of the straight line fit, minimum departure from linearity will ensure accurate extraction of the desired data. It has recently been reported [14] that the highest degree of linearity is given by the last of the above-mentioned plots, which is about twice as good for the second approximation as for the first. The best approximation, however, is when log g(α) is divided by squared temperature [1, 14].

The choice of the functions $g(\alpha)$ depends on the purpose of our kinetic study. In heterogeneous processes three basic elementary events can always be distinguished: (1) transport of reacting species to or from the reaction zone (diffusion), (2) formation of energetically-favorable domains of the product (nucleation); (3) incorporation of reacting species into the newly-formed phase-boundary of the product (interface reaction). Nucleation is usually followed by crystal growth, controlled by diffusion and/or interface reaction [15]. The overall kinetics can then be described by the function $g(\alpha) = [-\ln(1-\alpha)]^p$, where the exponent p is equal to 1/4, 1/2, 1/3, 3/4, 2/3 and 1 (symbols A1, A2, A3, A4, A5 and F1, respectively), depending on the nucleation rate, nucleus shape etc. [1, 15]. For the interface reaction the relation $g(\alpha) = [1 - (1-\alpha)^{1/3}]^n$ holds, where $n = 1/2$ and 1/3 for two and three-dimensional symmetry (symbols R2 and R3), respectively. Diffusion is expressed by the simplest forms of the functions, which do not account for e.g. the differences in the volume of the reactant and the product, i.e.

$$g(\alpha) = (1-\alpha)\cdot\ln(1-\alpha) + \alpha\ (D1),$$
$$(1-(1-\alpha)^{1/3})^2\ (D2),\ ((1+\alpha)^{1/2}-1)^2\ (D3),$$
$$2/3\,(1-\alpha) - (1-\alpha)^{2/3}\ (D4)\ \text{and}\ (1/(1-\alpha)^{1/3}-1)^2\ (D5).$$

It is clear that the plot of log $g(\alpha)$ vs. $1/T$ cannot distinguish the value of the exponent p, as it forms part of the straight line slope; nor is it possible to separate the diffusion $D2$ from the interface reaction $R3$. The calculated activation energy is thus the product of the true activation energy and the corresponding exponent. Their refinement can be made through the most reliable value of the preexponential factor calculated in parallel, [16], or better, by consideration of complementary evidence. Valuable assistance can be provided by the differential method of kinetic data calculation [17–18], because the differential forms of the functions $g(\alpha)$ become analytically distinguishable. It must be emphasized that, owing to the small differences and frequent overlaping between the values of the individual case-models, no analysis can be completely unambiguous, and hence the final decision always rests upon the investigator's logic-computer evaluation that assists in reducing time-consuming evaluation and may even lead to a preliminary classification of the results.

Description of the program

The program flowchart is given in Table 1. From the input data, either DTA or TG, the non-dimensional conversional transformation $\alpha(0 \leq \alpha \leq 1)$ is calculated (in DTA being equivalent to the simple ratio of partial to total peak area [5, 19], together with corresponding values of the reciprocal temperature and the $-\log g(\alpha)$ functions for nineteen preselected rate-controlling processes. After the calculation of the intermediate values the entire evaluation is carried out on the basis of two criteria:

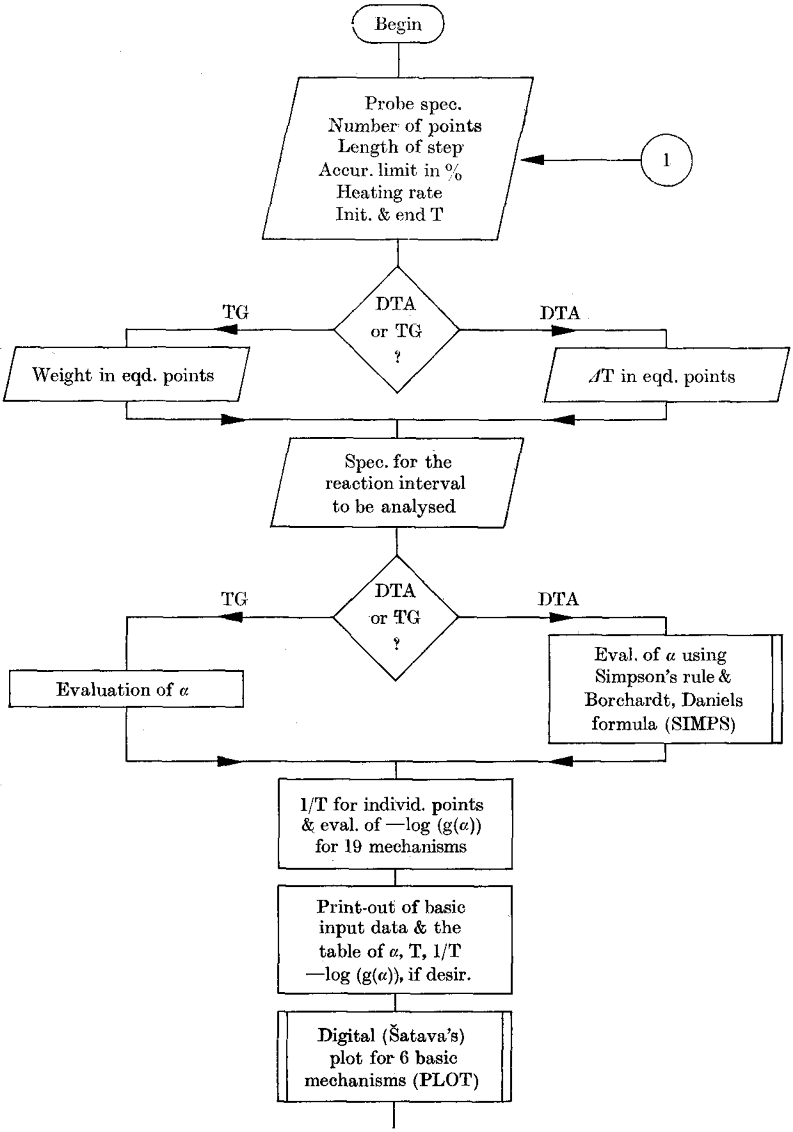
(1) the extent of the linearity region in which the dependence $-\log g(\alpha)$vs. $1/T$ lies within the preselected α limit; and

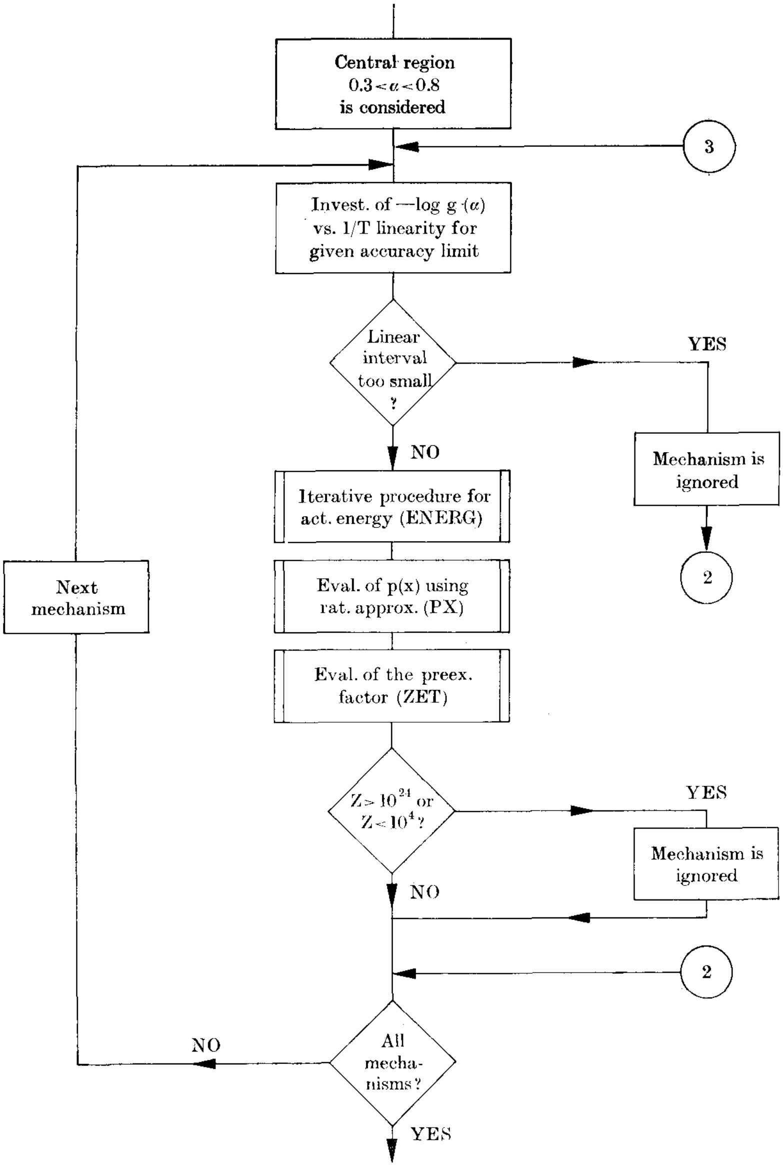
(2) the extent of the standard deviation calculated for the linearity region.

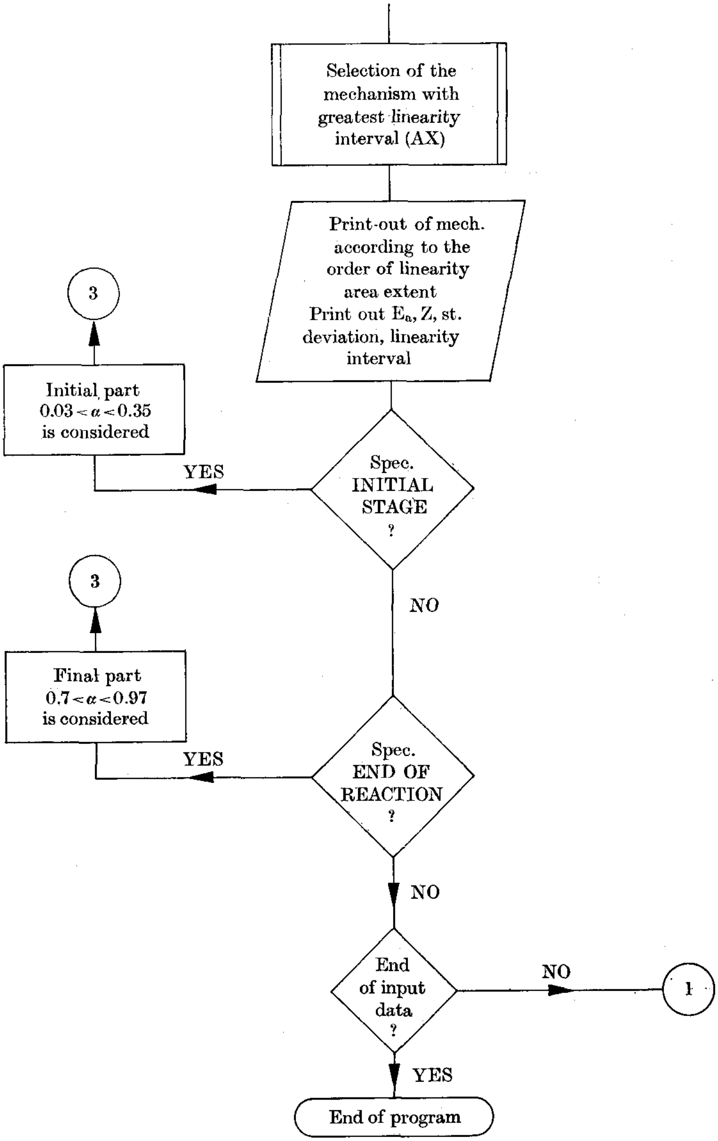
The establishment of the greatest linearity region of the straight line fitting (subroutine VYP) is accomplished after trial-and-error for the preselected, input region in α. In our experience three regions are to be considered; the main (intermediate), for (α 0.3–0.8); the initial (0.03–0.35); and the final (0.7–0.97). Roughly evaluated straight lines within these regions serve to check all points within and near the interval. The points which deviate more than permitted by a preselected limit are neglected, and the points which still fit well are included. For final calculation of the straight line slope, tan β, only the part lying within the given linearity region is considered. The standard deviation τ is also calculated only within this region. The mechanism where the calculated region of linearity is less than that initially required is neglected. For the remainder the activation energy, E, is calculated (function ENERG) employing a method of successive approximations. Input data are taken as $X = 2.03 \tan \beta(\bar{T})$ (where $\bar{T}$ is taken as the temperature at $\alpha = 0.5$) and E is calculated by an iterative procedure [8, 12], assuming that $E = 1.986$ e*p(x)tan β. The function p(x) is calculated by means of three formulae [21] for three different areas of $x(= E/RT)$, with an error less than 10^{-7}. The iteration procedure is completed when two consecutive values agree within 90 cal, is halted after twenty loops. The preexponential factor Z is calculated by back-substitution into the original kinetic equation [6, 8, 12]. The value of Z serves as a second criterion [16] to exclude less probable mechanisms, particularly those where Z falls outside the interval [22] $10^{24} > Z > 10^4$. Final ordering of so far acceptable mechanisms is made separately for the individual input regions of α according to the extent of linearity. The print-out includes the mechanism specification (M) the activation energy (E), the preexponential factor (Z) the standard deviation (σ) and the extent of linearity (%) (see Table 2). A complementary graphical printing of six basic $g(\alpha)$ functions ($D1$, $D4$, $D5$, $R2$, $R3$ and $F1$) is also included. One can also

Table 1

Flowchart of the program




Central region
$0.3 < \alpha < 0.8$
is considered
3
Invest. of —log g (α) vs. 1/T linearity for given accuracy limit
Linear interval too small ?
YES
NO
Mechanism is ignored
2
Iterative procedure for act. energy (ENERG)
Next mechanism
Eval. of p(x) using rat. approx. (PX)
Eval. of the preex. factor (ZET)
$Z > 10^{24}$ or $Z < 10^{4}$?
YES
Mechanism is ignored
NO
2
NO
All mechanisms?
YES


Selection of the mechanism with greatest linearity interval (AX)
Print-out of mech. according to the order of linearity area extent
Print out E_a, Z, st. deviation, linearity interval
3
Initial part
$0.03 < \alpha < 0.35$
is considered
YES
Spec. INITIAL STAGE ?
NO
3
Final part
$0.7 < \alpha < 0.97$
is considered
YES
Spec. END OF REACTION ?
NO
End of input data ?
NO
1
YES
End of program

choose an alternative print of the $-\log_{10}g(\alpha)\cdot$ vs. $1/T$ table for possible manual refinement.

The program is designed to evaluate series of thermoanalytical runs, the time for one curve-fitting amounting to about 5 sec with an IBM 370/145 computer. The program (in Fortran 4H level language) requires about $7\cdot 10^4$ bits and at present is part of the standard library for IBM 370/145 computers in the authors Institutes.

Discussion

The accuracy (i.e. the degree of precision with which the kinetic parameters E and Z are determined) and the correctness, $g(\alpha)$, (whether these kinetic parameters are attributed to the true rate-controlling process) of the resulting data depend above all upon the reliability of the input data. The smaller the accuracy in experimental scan, the greater the number of mechanisms evaluated, with greater dispersity in E and Z. Decrease in the number of scanned points may also result in the greater scatter of the resulting data (usually when below 20).

In order to test this program we have employed well-defined, theoretically-calculated curves (see Fig. 1) on which a normal scanning procedure was applied. The first two curves are simple cases of diffusion and nucleation, while the third

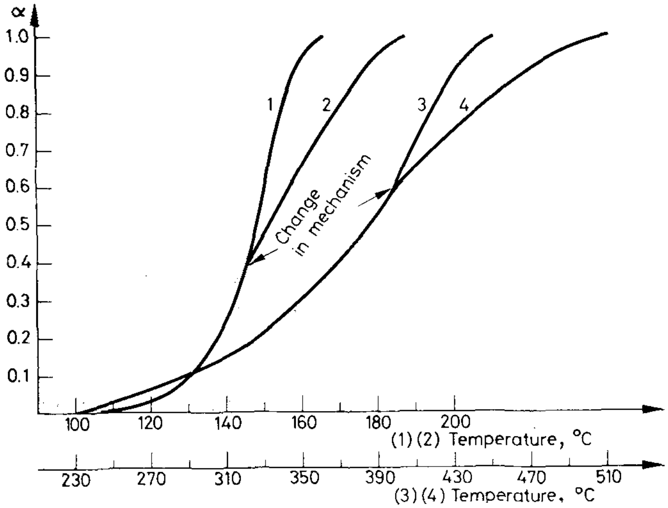


Fig. 1. Theoretical curves for most common heterogeneous processes with solids. Simple processes of nucleation (1), where $g(\alpha)_N = [-\ln(1-\alpha)]^{1/2}$ (A2) and diffusion (3), where $g(\alpha)_D = [1-(1-\alpha)^{1/3}]^2$ (D2). (2) Process controlled by nucleation (N) up to $\alpha = 0.4$, where diffusion (D2) becomes the rate-controlling process. (3) Process determined by diffusion (D2), but at $\alpha = 0.6$ there is a change of kinetic parameters $(E_D, Z_D \rightarrow E'_D, Z'_D)$

Table 2

Resulting data listed by computer

Theoretical curve	accuracy limit	central region $0.3 < \alpha < 0.8$				
		M	E	Z	%	σ
$0<\alpha<1$ D2 (Jander) $E = 18$ $Z = 10^9$	7%	D4	18.1	$8 \cdot 10^9$	83	0.024
		D2	19,3	$7 \cdot 10^9$	84	0.025
		D1	17.5	$2 \cdot 10^9$	75	0.038
	12%	D2	19.2	$7 \cdot 10^9$	90	0.032
		D3	14.7	$3 \cdot 10^6$	87	0.053
		D4	18.6	$2 \cdot 10^{10}$	87	0.057
		D5	21.2	$2 \cdot 10^{11}$	77	0.066
$0<\alpha<1$ A2 (Avrami, $p = 1/2$)	7%	A2	19.0	$3 \cdot 10^8$	62	0.062
		A5	25.9	10^{12}	62	0.062
		A4	29.3	$7 \cdot 10^{13}$	62	0.062
		F1	39.6	$2 \cdot 10^{19}$	62	0.062
		R3	37.1	$3 \cdot 10^{17}$	78	0.13
$E = 18$ $Z = 10^8$	12%	A2	18.4	10^8	96	0.12
		A5	25.0	$5 \cdot 10^{11}$	96	0.12
		A4	28.3	$3 \cdot 10^{13}$	96	0.12
		F1	38.4	$6 \cdot 10^{18}$	96	0.12
		R3	36.7	$2 \cdot 10^{17}$	86	0.097
At $\alpha = 0.4$ change A2 $0<\alpha \leq 0.4$ $E = 18$ $Z = 10^8$	7%	F1	17.0	$2 \cdot 10^7$	60	0.07
		D5	41.8	$2 \cdot 10^{19}$	53	0.04
		D3	18.7	$5 \cdot 10^6$	53	0.03
D2 $0.4 < \alpha < 1$ $E = 28$ $Z = 2.2 \cdot 10^{10}$	12%	F1	17.4	$5 \cdot 10^7$	65	0.16
		D3	18.9	10^6	65	0.043
		D5	45.2	10^{21}	64	0.11
		D4	28.3	$2 \cdot 10^{12}$	62	0.051
At $\alpha = 0.6$ change D2 $0 < \alpha \leq 0.6$ $E = 25$ $Z = 6 \cdot 10^5$	7%	D5	30.3	10^5	53	0.04
D2 $0.6 < \alpha < 1$ $E = 38$ $Z = 5.7 \cdot 10^{10}$	12%	D5	32.5	$5 \cdot 10^5$	58	0.04

for the evaluation of curves in Fig. 1

initial part $0.03 < \alpha < 0.35$					final part $0.7 < \alpha < 0.97$				
M	E	Z	%	σ	M	E	Z	%	σ
D2	18.8	$4 \cdot 10^{9}$	94	0.033	D2	18.0	10^{9}	54	0.042
D4	18.1	$7 \cdot 10^{8}$	76	0.016	F1	11.6	10^{7}	29	0.019
D1	18.0	$3 \cdot 10^{9}$	58	0.022					
D3	16.6	$6 \cdot 10^{7}$	53	0.023					
D2	19.0	$5 \cdot 10^{9}$	96	0.074	D2	18.4	$2 \cdot 10^{9}$	96	0.036
D4	18.7	$2 \cdot 10^{9}$	84	0.044	D4	13.9	10^{6}	51	0.051
D1	18.6	$7 \cdot 10^{9}$	68	0.058	F1	11.4	$6 \cdot 10^{5}$	47	0.047
D3	17.3	$2 \cdot 10^{8}$	63	0.041	D5	34.7	10^{20}	33	0.034
R3	36.7	$2 \cdot 10^{17}$	86	0.11	A2	18.4	10^{8}	96	0.12
R2	36.8	$3 \cdot 10^{17}$	67	0.11	A5	25.0	$5 \cdot 10^{11}$	96	0.12
A2	18.8	$2 \cdot 10^{8}$	36	0.13	A4	28.3	$3 \cdot 10^{13}$	96	0.12
A5	25.6	$7 \cdot 10^{11}$	36	0.13	F1	38.4	$6 \cdot 10^{18}$	96	0.12
A4	29.0	$7 \cdot 10^{13}$	36	0.13	D3	18.9	$6 \cdot 10^{7}$	27	0.012
R3	36.7	$2 \cdot 10^{17}$	86	0.1	A2	18.6	10^{8}	97	0.14
R2	36.4	$2 \cdot 10^{17}$	78	0.13	A5	25.4	$6 \cdot 10^{11}$	97	0.14
A2	18.6	$2 \cdot 10^{8}$	46	0.051	A4	28.8	$5 \cdot 10^{13}$	97	0.14
A5	25.4	$6 \cdot 10^{11}$	46	0.051					
A4	28.8	$5 \cdot 10^{13}$	46	0.051					
R3	34.5	$6 \cdot 10^{15}$	36	0.021	D2	28.1	$6 \cdot 10^{10}$	60	0.019
R2	34,2	$6 \cdot 10^{15}$	36	0.021	D4	22.3	$6 \cdot 10^{8}$	50	0.017
A2	16.8	$2 \cdot 10^{7}$	36	0.03	D1	18.2	$2 \cdot 10^{7}$	30	0.033
A4	26.0	$2 \cdot 10^{12}$	36	0.03	F1	17.9	10^{7}	71	2.14
A5	22.9	10^{10}	36	0.03					
R3	34.0	$4 \cdot 10^{15}$	41	0.026	D2	29.2	$3 \cdot 10^{10}$	65	0.035
R2	33.6	$4 \cdot 10^{15}$	41	0.037	D4	23.6	$7 \cdot 10^{8}$	60	0.037
A2	17.0	$2 \cdot 10^{7}$	36	0.031	D1	18.7	$4 \cdot 10^{7}$	40	0.12
A5	22.9	$2 \cdot 10^{10}$	36	0.031	F1	17.9	10^{7}	71	2.14
A4	26.0	10^{12}	36	0.031					
D5	27.2	10^{6}	49	0.01	D2	36.6	$6 \cdot 10^{9}$	53	0.04
D2	24.0	10^{6}	48	0.02					
D5	27.0	10^{6}	51	0.01	D2	36	$6 \cdot 10^{9}$	56	0.04
D2	24.0	10^{6}	48	0.02					

curve is the most common case of a combined process: nucleation followed by diffusion. The fourth curve is the synthesis of two consecutive diffusion processes as found in practice (oxidation of CaO [17]). The number of read-out points was 25 for the simple curves and 35 for the complex curves. The accuracy limit of the straight line fitting was chosen above (12%) and below (7%) the usually reported error of the kinetic parameters (±10%).

The computed data are listed in Table 2, from which it follows that:

1) Diffusion mechanisms are rated only after consideration of all criteria applied with the values of *E* in the region of 18 ± 2 kcal. Despite the slight differences between the analytical forms of the individual diffusion mechanisms, the model relation *D*2 is generally, in first place. The deviation of *E* from the theroetically inserted value lies within the normal region.

2) The case of nucleation and consequent crystal growth yields more complex data where it is not possible to distinguish directly between *A*2, *A*4 and *A*5, although model *A*2 gives kinetic parameters corresponding to the theoretically inserted ones. The steeper course of the curve (less accurate scanning) is reflected

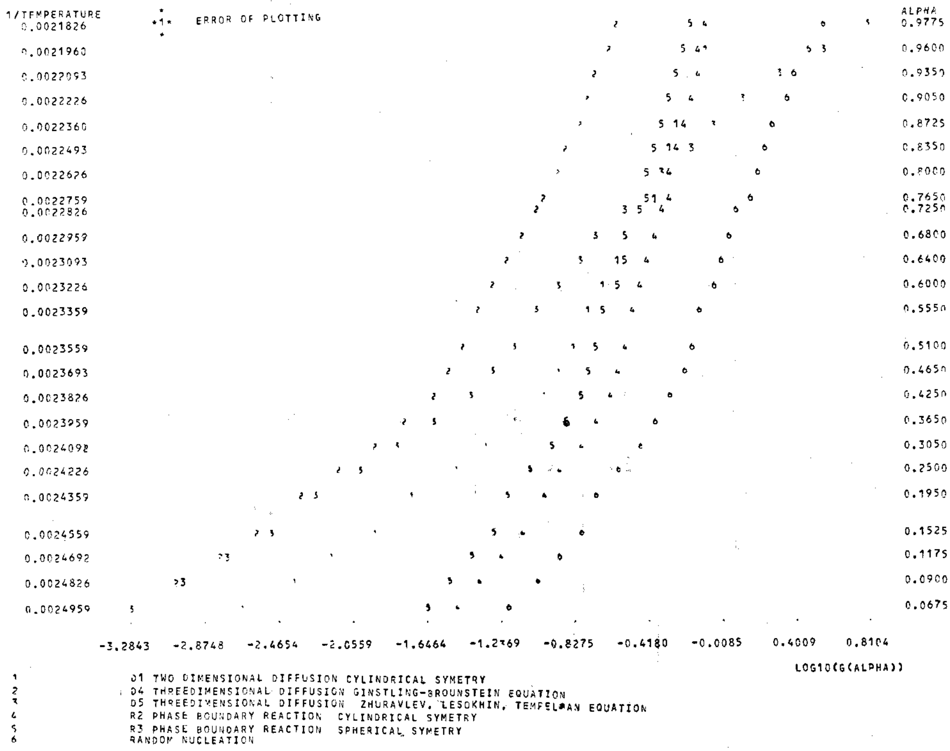


Fig. 2. Numerical print-out of Šatava's plot by IBM 370/145 computer evaluating curve (2), see Fig. 1

in the greater dispersion of the resulting data, particularly in the initial part, where the interface models $R2$ and $R3$ are preferred.

3) Interesting results are obtained for the case where the rate-controlling process changes during the course of the process as illustrated by sharp breaks in the plots $-\log_{10}g(\alpha)$ vs. $1/T$ (see Fig. 2). Such a break may serve as the first indication of a combined case, where attention should predominantly be focussed on the initial and final parts of the process. In the central region the least sensitive function (double logarithm) is fitted within only 60% (E being close to the theoretical), whereas the final part of the curve is unambiguously described as diffusion-controlled. The initial part yields the interface reactions $R2$ and $R3$ as most probable, but on comparing the kinetic parameters of the final part ($0.31 < \alpha < 0.96$, $D2$, $E = 28.1$ and $Z = 6 \cdot 10^{10}$) with those of the initial part ($0.01 < \alpha < 0.42$; $R3$, $E = 34.5$ and $Z = 6 \cdot 10^{15}$) we can see that both E and Z decrease from the advancing to the terminating part of the process. This is in contradiction with the theoretically-introduced change in the mechanism, which brings the increase of E and Z in order to match the values of the two models. It can also be understood from mathematical analysis [1, 25]. Hence the nucleation-determined process, A, should be preferred, namely $A2$ with E and Z lying below those for $D2$ (and $D4$).

4) The last case demonstrates the condition where the diffusion mechanism is altered during the process, as is unambiguously classified in the output data.

It can be seen that the program cannot distinguish between the individual cases of nucleation-growth limited processes, for which a derivative method is more sensitive and should thus be additionally applied [20, 23, 24]. The differences between the A and R types of rate-controlling processes are not easy to establish precisely.

Attention should be paid to the processes in the vicinity of equilibrium, because close to the equilibrium temperature linear proportionality between $-\log g(\alpha)$ and $1/T$ does not hold [16]. In such a case the final part of the process should be considered preferably.

The degree of the preselected accuracy limit within which the straight line fit of $\log g(\alpha)$ vs. $1/T$ is calculated should not be put too low (usually not below 5%).

For the straight line slope calculation the least-squares method was employed in the form of a simple linear equation. This, however, is correct only in the case of the Gaussian distribution of both variables, but in the case of the plot $-\log g(\alpha)$ vs. $1/T$ this is not completely fulfilled. However, for the small interval of scanning the experimental error usually becomes greater than that introduced by equidistant temperature scanning, so that more adequate iteration loops aimed at minimum deviation are not needed.

Conclusion

It is not possible to expect that a computer evaluation yields results not requiring further treatment. The above algorithm provides maximum information concerning the more probable mechanisms, and excludes the less probable ones, using the following criteria:

1) the interval of linearity for the $-\log g(\alpha)$ vs. $1/T$ plot;
2) the value of the standard deviation within this region;
3) the value of the preexponential factor.

The program cannot distinguish between the individual cases of nucleation-determined mechanisms. In the classification of combined processes, the initial and the final regions are considered most important, where the increase of E and Z with the change of rate-controlling process appears more probable.

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Résumé — On discute la possibilité d'appliquer la méthode d'intégration de Šatava à la description cinétique des processus hétérogènes étudiés en conditions anisothermes. On trouve que cette méthode manque de sensibilité pour distinguer les différents modèles de germination et croissance. Cet inconvénient est souligné par des critères supplémentaires comme l'intervalle de l'ajustement linéaire, l'écart-type et la valeur du facteur pré-exponentiel.

On explique l'algorithme pour les opérations mathématiques nécessaires. On discute le système d'impression graphique sous forme d'une fonction numérique valable pour tous les ordinateurs. Le programme est utilisé dans le cas de plusieurs processus. Il permet une classification préliminaire des processus en indiquant si ceux-ci sont possibles ou non. Il permet aussi de déceler les changements de mécanismes réactionnels par l'analyse séparée de trois étapes consécutives du processus.

ZUSAMMENFASSUNG — Einleitend wird die Anwendbarkeit von Šatava's Integralmethode zur kinetischen Beschreibung nichtisotherm geprüfter heterogener Prozesse erörtert. Die Methode wird für nicht genügend empfindlich gehalten um zwischen verschiedenen Typen von Kernwachstumsmodellen zu unterscheiden. Dieser Nachteil wird durch Anwendung zusätzlicher Kriterien, wie lineare Anpassung, Streuungswerte und Wert des präexponentiellen Faktors noch mehr betont. Der Algorithmus für die notwendigen mathematischen Operationen wird erklärt. Ein graphischer Ausdruck in der Form einer für jeden Komputer zugänglichen Funktion wird erörtert. Die Anwendbarkeit dieses Programs wird an Hand verschiedener Prozesse geprüft. Das Program erwies sich als geeignet für vorhergehende Klassifizierungsprozesse, sowie zur Erfassung von Änderungen im Reaktionsmechanismus durch einzelne Analysen dreier aufeinanderfolgender Teile des Prozesses.

Резюме — Впервые обсуждена применимость интегрального метода Шатавы для описания кинетики неизотермических гетерогенных процессов. Найдено, что этот метод нечувствительный, чтобы отличить различные типы моделей образование-рост центров кристаллизации. Этот недостаток устраняется использованием таких дополнительных критериев как интервал прямая-вертикаль-сборка, стандартное отклонение и значение предэкспоненциального фактора. Объяснен алгоритм необходимых математических операций. Особое ударение сделано на то, что графическое печатание представляется в числовой форме, что доступно для каждой вычислительной машины. Применимость этой программы проверена на различных процессах. Показано, что программа подходит для предварительной классификации процессов как более, так и менее приемлемых, а также для обнаружения изменений в механизме реакций, раздельным анализированием трех последовательных частей такого процесса.