

## Original papers

A METHOD FOR EVALUATING THE PARAMETERS  
 ● OF A UNIVERSAL KINETIC MODEL OF A POLYREACTIVE  
 REACTANT FROM DATA ON ISOTHERMAL COURSE  
 OF A HETEROGENEOUS REACTION

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*A model system of  $\alpha - t$  (conversion — time) data on isothermal course of a heterogeneous reaction was used to derive a procedure for determining the parameters of an equation for a universal kinetic model of a polyreactive reactant*

$$\alpha = \sum_{j=1}^m x_j \alpha_j$$

*on the condition that*

$$\alpha_j = 1 - \exp(-r_j t),$$

*where  $r_j$  is a parameter expressing the reactivity of a homoreactive fraction whose content in the reactant in question is  $x_j$ .*

*The method is based on determining the minimum sums of deviations squared (MSDS) and thus the optimum values of the parameters at gradually increasing number  $m$  of the equation terms. Equalization of MSDS is a criterion for the effective value of  $m$ . As parameters of the model are then regarded those values which describe adequately the given  $\alpha - t$  relationship with the use of the effective number  $m$  of homoreactive fractions.*

### INTRODUCTION

Solid-state reactions constitute the basic element of technological processes in commercial production of inorganic materials. The aim of studying the reactions is to learn their kinetics and to utilize the knowledge for the purpose of intensifying effectively the respective process, first of all its controlling stage. If the reaction mechanisms are unknown or even for the sake of simplicity, relationships derived from kinetic models (formal kinetics) are often used to describe their course.

#### Universal kinetic model of a polyreactive reactant

The classical kinetic models were mostly created on the assumption that the particle of the reactant is situated in a continuous homogeneous medium of an excess of the other reactant, that it can be regarded as a geometrically simple body and that it can be considered to be energetically homogeneous with respect to its reactivity. The models usually did not take into account other parameters of the reactant such as the distribution of its particles in the reaction mixture,

the particle size distribution, the complexity of their shape and above all their energetical inhomogeneity. Although in some instances the equations yielded by such models describe acceptably the changes of quantities characterizing the course of the reaction (most frequently the time dependence of conversion of the reactant, or its temperature dependence), the width of their applicability was quite limited. Extensive utilization of these equations in the description of processes where the assumptions of their derivation are demonstrably not met, tends to degrade them to mere empirical regressive relationships and there is no reason to believe that they provide any information on the mechanism of the respective process.

In 1973, Jesenák [1] suggested a universal kinetic model that eliminated some of the drawbacks of the previous models, being based on the assumption of reactivity distribution. According to the model the reactant is a polyreactive substance and the reaction units (kinetic particles) whose reactivities, i.e. manifestations during the reaction, are identical (wherever they might be distributed in the reaction space) thus form the so-called phenomenological homoreactive (PH) fraction of the reactant. Although the reactivity distribution of the reactant is assumed to be continuous, owing to the possible division of each reactant into phenomenological proportions with approximately the same reactivity within the framework of each proportion (homoreactive fractions), the general form of the equation for a polyreactive reactant (MPR)\* can be written in the form

$$\alpha = \sum_{j=1}^m x_j \alpha_j \quad (1)$$

where  $\alpha$  is the fraction of conversion of the reactant as a whole, at time  $t$ ,

$x_j$  is the portion of the  $j$ -th PH-fraction in the reactant,

$m$  is the number of phenomenological homoreactive fractions.

Equation (1) is formally identical with the basic Sasaki's equation [3] (polydispersion kinetic model). In contrast to the latter, however,  $x_j$  signifies the portion of  $j$ -th phenomenological homoreactive fraction of the reactant and not the granulometric one. Similarly to Sasaki's model it holds, of course, that the sum of  $x_j$  fractions is equal to unity.

Sasaki proposed to express the conversion of each fraction in terms of time  $\alpha_j = f_j(t)$  in a standard way by the Valensi—Carter equation [4, 5]:

$$\frac{z}{z-1} - \frac{1}{z-1} [1 + \alpha_j(z-1)]^{2/3} - (1 - \alpha_j)^{2/3} = k_j t \quad (2)$$

where  $z$ ,  $k_j$  are parameters.

Such a requirement does not arise with the polyreactive reactant model; reaction path of each PH fraction can be described by an arbitrary suitable growth function  $f_j(t)$  [2, 6].

The polyreactive reactant model is a phenomenological model of a statistical system where a process with a complex mechanism takes place. In spite of this, not even this model provides information on the process mechanism. It demonstrates its effectiveness mainly in correlation of its parameters (or its statistical mo-

\*) Jesenák calls his model' relaxation polyreactive kinetic model (RPKM), regarding the reaction as elimination of thermodynamic stresses in the reaction system (for details refer e.g. to [2]).

ments) with the pre-history of the reactant (time of grinding, conditions of heat treatment, etc.), reaction mixture preparation (homogenization, compacting pressure, etc.) and the conditions of the reaction (temperature, pressure, composition of the atmosphere, etc.).

### Concretizing the analytical form of the MPR equation

Application of a certain classical kinetic model to description of an experimental time dependence of conversion represents in fact the task of finding also the model parameters, if they exist, so that the resulting equation would adequately and acceptably describe the given relationship. The term acceptable description is usually understood to mean such a model relationship from which the experimental points do not deviate by more than the maximum actual measuring error, i.e.  $3s$ , where  $s$  is the standard deviation of the individual measurements (a sufficient condition). With such an acceptability condition, a problem for only one model may have an infinite number of solutions, and even several kinetic models can be expected to conform to the given acceptability criterion. At the same time it is obvious that the following necessary condition will hold for the sums of deviations squared of all the acceptable relationships:

$$\left(\sum_{i=1}^n \Delta_i^2\right)_{\text{acc}} < 9 ns^2, \quad (3)$$

where  $n$  is the number of experimental data,  
 $\Delta_i$  is the deviation of an individual measurement.

The suitable kinetic models should be selected on the basis of the form of the experimental relationship and of the properties of functions following from the individual models. Among the acceptable relationships, further attention is usually paid to that considered optimal with respect to some criterion (usually the sum of deviations squared). In evaluating practice, the approach is quite the opposite: the optimum relationship is first found for the criterion selected, and only then the intervals of parameters, for which the relationships are acceptable, are determined.

Whereas with the classical models the analytical forms of their kinetic equations are unambiguously defined, the form of the equation is not precisely specified in the case of the model of a polyreactive reactant, as this depends on the form of functions  $\alpha_j = f_j(t)$ . Their form again depends on the evaluator's approach, because a single reactant can be modelled in several ways.

From the standpoint of subsequent evaluation of the parameters of the individual PH fractions, however, it is convenient to model the reactant by means of fractions whose reaction path can be described by function  $\alpha_j = f_j(t)$  of identical analytical form. Having chosen the form of this function, the problem of concretizing the kinetic equation is transformed into one of determining the number of its terms  $m$ . With increasing number of terms, the description of the experimental relationship will obviously be precisioned, and starting with a certain effective number  $m$ , all of the additional equations will be acceptable for certain intervals of their parameter values. A higher number of terms in equation (1) will therefore yield a smaller sum of deviations squared, but from the standpoint of reproducibility of experimental values, the results will be equivalent with those already obtained by means of the first (optimum) acceptable model rela-

tionship. From this it follows that the use of numbers of terms higher than the optimal one is not effective, and moreover the accuracy of the estimated parameters decreases with increasing  $m$ .

In evaluations of the  $\alpha = f(t)$  relationships free of inflexions, convenient use was made of the  $\alpha_j$  growth function in the form

$$\alpha_j = 1 - \exp(-r_j t), \quad (4)$$

where  $r_j$  is a parameter expressing the reactivity of  $j$ -th PH fraction of the reactant.

The present paper had the aim to derive a simple procedure for determining the number of terms  $m$  of the first acceptable model relationship on the assumption that the reaction paths of the individual fractions are described in a standard form given by equation (4).

#### DETERMINING THE NUMBER OF TERMS IN EQUATION MPR

The method for determining the minimum required number of terms for equation (1) was derived in a model system whose data were calculated by means of Jander's equation in the form (theoretical relationship)

$$\alpha = 1 - (1 - \sqrt{1 \times 10^{-5} t})^3. \quad (5)$$

In the literature, Jander's equation is often successfully used to describe experimental relationships of conversion in terms of time.

The times  $t$  for which the conversion values were calculated, were first determined from Jander's equation in the form

$$t = 1 \times 10^3 (1 - \sqrt[3]{1 - \alpha})^2 \quad (6)$$

for  $\alpha = 0.04i$ , where  $i \in \{1, 2, \dots, 24\}$ , and rounded to one decimal, thus covering, with respect to conversion values, the entire range with an approximate spacing of 0.04 between the points. For the times obtained, the 'theoretical' values of conversion were calculated and loaded with the generated random error in the third decimal place ('experimental' values). The rounding up of the times and adjustment of the conversion values were chosen so as to correspond to the accuracy of a standard experiment. The times  $t$  and the 'experimental' values of the model system are listed in Table I and in part plotted in Fig. 1.

The 'experimental' values of conversion showed absolute deviations  $|A_i|$  from the theoretical ones over the interval of  $9.1 \times 10^{-3}$  to  $2.1 \times 10^{-6}$  with a mean absolute deviation  $|\bar{A}| = 4.1 \times 10^{-3}$ . The sum of deviations squared of 'experimental' points from the 'theoretical' relationship was  $0.626 \times 10^{-3}$ , and the calculated standard deviation, on the assumption of normal distribution of the measuring error and equal dispersion over the entire interval measured was

$$s = \sqrt{\frac{0.626 \times 10^{-3}}{24}} = 5.1 \times 10^{-3}. \quad (7)$$

From this it follows that as acceptable model relationships one can regard all those whose deviation of points does not exceed the value  $3s = 15.3 \times 10^{-3}$  and the sum of deviations squared is smaller than  $9ns^2 = 5.63 \times 10^{-3}$ .

**Table I**

The model set and its deviations from MPR equations for  $m = 1-4$

$i$	$t/\text{min}$	$10^3 \alpha_{\text{exp}}$	$10^3 \Delta_1$	$10^3 \Delta_2$	$10^3 \Delta_3$	$10^3 \Delta_4$
1	0.2	42	-39	-30	-18	-0
2	0.8	82	-71	-37	-4	2
3	1.7	121	-97	-33	6	-4
4	3.2	156	-111	-8	14	5
5	5.1	208	-138	-3	-5	-5
6	7.6	246	-143	12	-9	-2
7	10.7	276	-134	28	-2	6
8	14.5	314	-127	28	0	5
9	19.1	363	-125	11	-7	-6
10	24.5	405	-110	-1	-6	-9
11	30.9	431	-75	3	10	5
12	38.4	472	-51	-5	10	5
13	47.1	520	-31	-19	1	-2
14	57.3	566	-8	-27	-5	-7
15	69.3	592	35	-13	7	8
16	83.3	640	55	-18	-3	-1
17	99.9	675	84	-8	0	4
18	119.5	719	99	-5	-4	-1
19	143.3	766	104	-4	-11	-8
20	172.4	795	119	14	2	3
21	209.0	837	112	19	2	1
22	256.8	880	94	20	1	-1
23	323.9	920	70	20	3	-1
24	433.0	954	44	20	7	4

**Table II**

Characteristics of MPR equations for  $m = 1-4$  (SDS — sum of deviations squared)

$m$	$x_j$	$r_j/\text{min}^{-1}$	$10^3 \text{ SDS}$	$ \bar{Z} $
1	1.000	$1.42 \times 10^{-2}$	213.677	0.087
2	0.283 0.716	$1.92 \times 10^{-1}$ $7.68 \times 10^{-3}$	8.807	0.016
3	0.128 0.263 0.610	$8.87 \times 10^{-1}$ $4.86 \times 10^{-2}$ $6.37 \times 10^{-3}$	1.253	0.006
4	0.050 0.129 0.255 0.567	5.33 $2.77 \times 10^{-1}$ $3.26 \times 10^{-2}$ $6.00 \times 10^{-3}$	0.526	0.004

The optimized relationships according to equations (1) and (4) were then plotted through the 'experimental' points while the number of terms of the sum was gradually changed ( $m = 1, 2, 3, 4$ ). The sum of deviations squared was employed as the optimizing criterion, the simplex method being used in the optimizing procedure. The calculation results (values of the optimum parameters, minimum sums of deviations squared and mean absolute deviations) are listed in Table II; deviations  $\Delta_{i1}$  through  $\Delta_{i4}$  of inversely calculated conversion values for  $m = 1 - 4$  are listed in Table I; the optimum relationships for various values of  $m$  are represented in Fig. 1.

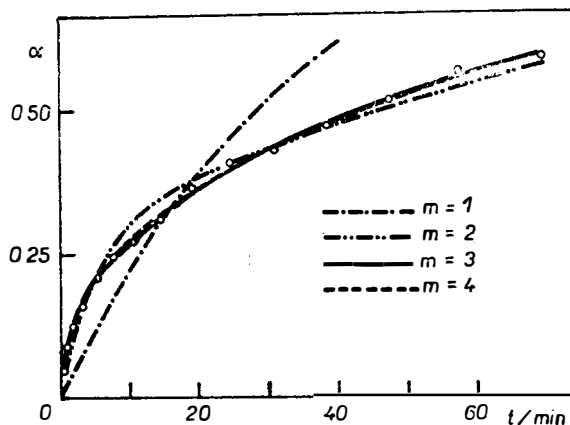


Fig. 1. Model set and the relationships following from MPR for  $m = 1 - 4$ .

Mere visual evaluation of the individual model relationships plotted in Fig. 1 shows that the curves with  $m = 1$  and  $m = 2$  are not acceptable for this model system. According to Table 2, the 'experimental' values in these two instances have mean absolute deviations  $|\bar{\Delta}|$  equal to 0.087 and 0.016 respectively, i.e. values higher by up to 20.9 and 3.9 respectively than the mean absolute deviation of the data system from the original 'theoretical' relationship (0.004). The minimum sums of deviations squared (MSDS) for these curves are also quite high ( $213,677 \times 10^{-3}$  and  $8,807 \times 10^{-3}$ ) and compared to the sum of deviations squared of the 'experimental' points from the 'theoretical' relationship ( $0.626 \times 10^{-3}$ ) they are higher by a factor of more than 9 (341.4 and 14.1 respectively).

In contrast to this, the third curve shows deviations of only  $\pm 0.006$  (higher 1.4 times), thus attaining the level of the original 'experimental' curve ( $|\bar{\Delta}| = 0.004$ ). The sum of deviations squared from the 'experimental' points is  $1.253 \times 10^{-3}$ , i.e. a value only double that of the sum of deviations squared of these points from the original relationship ( $0.626 \times 10^{-3}$ ). The deviations of points from this curve, with the exception of four points (17% of 'experimental' data), are of the order of  $10^{-3}$  and smaller; of the four cases mentioned, only one ( $\Delta_{13} = 17.9 \times 10^{-3}$ ) exceeds slightly the limit  $3s = 15.3 \times 10^{-3}$ . In view of the account given above, this model relationship already can be considered acceptable.

The model curve with  $m = 4$  exhibits still better parameters than the third one; its values are approximately identical with those of the 'theoretical' relationship. The curves with  $m = 5$  would obviously be also acceptable and provide still more favourable results.

On working with a real experimental system where the standard deviation value  $s$  is often unknown, one should take into account that the ratio of the minimum sums of deviations squared is the more sensitive of the characteristic data followed, as it tends to change at a higher rate.

The mutual ratio of consequent minimum sums of deviations squared at an gradually increasing value of  $m$  converges to the limit value of 1.0, and for the model system considered acquires the values  $\text{MSDS}_1 : \text{MSDS}_2 = 24.3$ ,  $\text{MSDS}_2 : \text{MSDS}_3 = 7.0$  and  $\text{MSDS}_3 : \text{MSDS}_4 = 2.4$ . All this shows that an acceptable equation with the lowest number of terms  $m$  is that optimized equation whose sum of deviation squared no longer changes significantly with further increasing the number of terms.

## DISCUSSION

For the model system considered, the first acceptable equation has therefore 3 terms which express a model of a reactant comprising three PH fractions. The fractions have representations of approximately 13, 26 and 61 % while their reactivities differ by an order of magnitude. This means in practice that the individual fractions take different parts in different stages of the reaction.

The fastest reacting fraction ( $r_1 \doteq 0.9 \text{ min}^{-1}$ ) reacts almost entirely (90 %) within about 2.6 min while the portions of the other two fractions in the overall conversion at that time are still relatively small (about 20 % and 6 % respectively). In this stage the overall course of the reaction is therefore described approximately by the reaction of the fraction reacting at the highest rate using the equation

$$\alpha = x_1[1 - \exp(-r_1 t)]. \quad (8)$$

In the following reaction stage the share of this fraction in the overall conversion is already almost constant, so that the time dependence of the conversion can be described by the approximate equation

$$\alpha = x_1 + \sum_{j=2}^3 x_j[1 - \exp(-r_j t)]. \quad (9)$$

A considerable proportion (75 %) of the fraction reacting at the medium rate ( $r_2 \doteq 5.0 \times 10^{-2} \text{ min}^{-1}$ ) will react within about 28.5 min and till that the other two fractions take a minor share in the conversion increment. During the stage when the contribution by the slowest fraction to the overall conversion increment is of small significance, the reaction can be described by the approximate relationship

$$\alpha = x_1 + x_2[1 - \exp(-r_2 t)]. \quad (10)$$

In the last stage of the reaction when the main share of the overall conversion increment is provided by the fraction showing the lowest reaction rate ( $r_3 \doteq 6.4 \times 10^{-3} \text{ min}^{-1}$ ), the basic equation can be analogously adjusted to the form

$$\alpha = x_1 + x_2 + x_3[1 - \exp(-r_3 t)]. \quad (11)$$

From the account it follows that such a modelling of the reactant divides the course of the reaction into  $m = 3$  stages (rapid start, a medium part and gradual conclusion) and that the values of overall conversion yield various information about the parameter values in different stages of the course of the reaction. For

example, in the given model case the reactivity  $r_1$  is determined above all by 'experimental' points up to 2.6 min, only three points, the  $r_2$  by five to six points over the time interval of 2.6—28.5 min, while the reactivity of the slowest fraction is given by about a double number of points.

The accuracy of determining the values of reactivity  $r_j$  can be said to depend substantially on the distribution of experimental points along the curve. For example, if the set would not include the first data, reactivity  $r_1$  could not be determined. In that case only the limit value of  $r_1$  could be determined, namely such a value for which equation (9) would describe the further course of the reaction. Similarly, if data from the last stage of the reaction were not available, it would only be possible to determine the limit value of  $r_3$  the effect of which could not have influenced the previous stages of the reaction.

More favourable conditions exist in the determination of values  $x_j$  which manifest themselves in all stages of the reaction (cf. equations 8, 9, 10 and 11). Possible absence of the first points thus does not hinder determination of  $x_1$  and the value of  $x_3$  can also be calculated additionally without any experimental data from the end of the reaction.

#### CONCLUSION

Application of the universal kinetic model of a polyreactive reactant to the description of relationships in the conversion of reactants in terms of time in the course of heterogeneous isothermal reactions allows a more complex characteristic of the reacting substance to be established (particularly with respect to reactivity distribution). In the simpler case the model serves to the fitting of conversion relationships without any restriction. Its multi-purpose character has been attained at the expense of simplicity of the equation, as also proved by the model set, where five parameters were necessary for describing a single-parameter relationship.

Possible further utilization of these parameters in the study of heteromogeneous reactions would require a simple reliable method for their determination. The submitted study demonstrates, on a model set of data, the possibility of resolving these problems under certain conditions. At the same time it points out the variability in the accuracy of parameters resulting from their number and relation to the individual stages of the reaction. In the authors' laboratory, the method for determining the parameters of the kinetic model is successfully utilized in the study of the kinetics of solid-state reactions.

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**METODIKA VYHODNOCOVANIA PARAMETROV UNIVERZÁLNEHO KINETICKÉHO MODELU POLYREAKTÍVNEHO REAKTANTA Z ÚDAJOV O IZOTERMICKOM PRIEBEHU HETEROGÉNNEJ REAKCIE**

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Univerzálny kinetický model polyreaktívneho reaktanta modeluje reaktanta pomocou fenomenologických frakcií (FH) s navzájom rôznou reaktivitou a pre prípad nespojitej distribúcie reaktivity poskytuje rovnicu v tvare

$$\alpha = \sum_{j=1}^m x_j \alpha_j,$$

kde  $\alpha$  je zlomok premeny (konverzia) reaktanta ako celku v čase  $t$ ,

$\alpha_j$  — konverzia  $j$ -tej FH frakcie v tom istom čase,

$x_j$  — podiel  $j$ -tej FH frakcie v reaktante,

$m$  — počet FH frakcií

Práca rieši problém určenia parametrov modelu na modelovom súbore  $\alpha - t$  údajov za predpokladu, že funkcie  $\alpha_j = f_j(t)$  majú jednotný tvar

$$\alpha_j = 1 - \exp(-r_j t),$$

kde  $r_j$  je parameter vyjadrujúci reaktivitu  $j$ -tej FH frakcie reaktanta.

Metóda spočíva v tom, že pri postupne sa zväčšujúcom počte členov  $m$  určuje vypracovaný výpočtový program minimálne súčty štvorcov odchýlok (MSSO). Ukázalo sa, že hodnota MSSO je takmer nemenná od takého  $m$ , pre ktoré spätne vypočítaná závislosť  $\alpha = f(t)$  už dobre fituje experimentálne údaje.

Parametre rovnice s efektívnym počtom členov  $m$  sa považujú za parametre modelu.

*Obr. 1 Modelový súbor a závislosti vyplývajúce z MPR pre  $m = 1 - 4$ .*

**МЕТОДИКА РАССМОТРЕНИЯ ПАРАМЕТРОВ УНИВЕРСАЛЬНОЙ КИНЕТИЧЕСКОЙ МОДЕЛИ ПОЛИРЕАКТИВНОГО РЕАКТАНТА НА ОСНОВАНИИ ДАННЫХ ОТНОСИТЕЛЬНО ИЗОТЕРМИЧЕСКОГО ХОДА ГЕТЕРОГЕННОЙ РЕАКЦИИ**

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Универсальная кинетическая модель полиреактивного реактанта моделирует реактант с помощью феноменологических фракций (FH) с взаимно разной реактивностью и в случае несвязанного распределения реактивности предоставляет уравнение в виде

$$\alpha = \sum_{j=1}^m x_j \alpha_j,$$

где  $\alpha$  — доля превращения (конверсии) реактанта как целого во времени  $t$ ,  $\alpha_j$  — конверсия  $j$ -ной FH фракции в том же времени,  $x_j$  — доля  $j$ -ной FH фракции в реактанте,  $m$  — количество FH фракций.

В предлагаемой работе решается проблема определения параметров модели на модельном наборе  $\alpha - t$  данных при предположении, что функции  $\alpha_j = f_j(t)$  имеют стандартный вид

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$$\alpha_j = 1 - \exp(-r_j t),$$

где  $r_j$  — параметр, выражающий реактивность  $j$ -той  $FH$  фракции реактанта.

Приводимый метод заключается в том, что при постепенно растущем количестве членов  $m$  устанавливает разработанная программа вычисления минимальные суммы квадратов отклонений (MSSO). Было доказано, что величина MSSO является почти неизменной с такого  $m$ , при котором обратно рассчитанная зависимость  $\alpha = f(t)$  уже хорошо согласуется с экспериментальными данными.

Параметры уравнения с эффективным количеством членов  $m$  считаются параметрами модели.

*Рис. 1. Модельный набор и зависимости, вытекающие из МПП для  $m = 1 - 4$ .*