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STATISTICAL ANALYSIS OF SOME TOPOCHEMICAL MODELS

N. A. CHERNOVA, I. V. ARKHANGEL'SKII and L. N. KOMISSAROVA

Department of Chemistry, Moscow State University, Moscow 117234, *USSR*

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A model process is considered in order to investigate the applicability of a particular statistical approach to determination of an input mechanism of topochemical reactions and of the relevant mathematical model.

It is shown that the analysis of the experimental data leads to different results due to the reproducibility errors. The applied statistical approach allows one to determine the input mechanism unambiguously when σ has the value of 0.01.

The kinetics of reactions involving solid compounds have received a great deal of attention during recent years. The methods used in handling heterogeneous processes differ considerably from those applied to homogeneous reactions.

Application of simple approximate models to the kinetics of topochemical reactions yields satisfactory results in quite a number of cases [1]. The use of specially-adjusted experimental techniques [2] often provides qualitative information about the reaction site and type of the reaction mechanism (that is, whether the reaction begins at nucleation centers or at all points of the surface simultaneously), as well as about some other important characteristics of the process. A variety of mathematical models, however, are consistent with each of the two mechanisms mentioned, and it is sometimes very difficult to choose between them [1]. The choice of the model which makes good physical sense poses even greater difficulties when the type of the reaction mechanism is unknown. The problem is of principal importance and represents a rather complicated statistical task.

In this paper, a model process is considered in order to investigate the applicability of a particular statistical approach [3] to determination of an input mechanism and of the relevant mathematical model. The latter had to be chosen from among a total of eleven equations of which only five were applicable to the type of mechanism in question. The model process analyzed was that of the reduction of zinc oxide with hydrogen: $ZnO + H_2 = Zn + H_2O$, which has been shown to begin at all points of the surface of the solid reagent simultaneously [2]. The "contracting-sphere" equation applies in this case, on the condition of homogeneous granulometric composition of the solid phase and of spherical (or nearly so) granules:

$$1 - (1 - \alpha)^{1/3} = kt \qquad (1)$$

For comparison, the following equations were chosen:

$$\text{type I: } 1 - (1 - \alpha)^{1-n} = kt \text{ where } n = 0,\ 1/2,\ 2/3,\ 3/4 \tag{2}$$

$$\text{type II: } \ln \frac{\alpha}{1 - \alpha} = kt + C \tag{3}$$

$$\text{type III: } \alpha = 1 - e^{-k't^m} \text{ where } m = 1,\ 2,\ 3,\ 1/2,\ 3/4 \tag{4}$$

Here α stands for the extent of conversion, t is time, k is the rate constant, and k' is the constant related to k by the equation

$$k = n(k')^{1/n} \quad (k = m(k')^{1/m}).$$

Lastly, $n(m)$ is the kinetic equation factor defined as the apparent reaction order.

The choice of these equations depended on a number of considerations. Type I equations can be fitted to any reaction proceeding via the mechanism in question, by adjusting the value of n; for systems with homogeneous granulometric composition, the value of n is apparently related to the shape of the granules. Note that with $n = 2/3$ Eq. (2) gives (1). The Prout–Tompkins equation (3) describes quite a different mechanism, involving a chain nucleation process. The Erofeev equation (type III) was chosen because of its general applicability: various m values correspond to quite different types of processes. Consideration of a greater number of mathematical models was deemed unnecessary.

The experiment was simulated by using the rate constants reported in the literature and determined from rate *vs.* temperature profiles [2]. The values chosen corresponded to seven temperature points in the range 795 to 855 K. Conversions α_i in the range 0.02 to 0.90 were calculated for each of the k_i values, using Eq. (1). The corresponding t_i values were taken at intervals of 1 min. Errors were introduced into the α_i values using the random numbers table and σ values of 0.01, 0.1 and 0.5. The thus-simulated experiment was analyzed using the 11 equations given above. Our task was to determine the best fitting one, evaluate the kinetic parameters with the help of the model chosen, and compare the results obtained with the literature data.

The properly-chosen model, when applied to experimental points, should give a straight-line dependence. In the first stage of the analysis, we selected the models that yielded linear-adequate dependences in the transformed coordinates. The usual F-test was not applied because of its low sensitivity, and the specially-designed statistical method [3] was used to determine small deviations from linearity.

It has been shown that the results depend strongly on reproducibility variance.

Thus, all the models give linear dependences with $\sigma = 0.5$. The noise proves too strong in this case even for discrimination between different types of mechanisms.

In the case of $\sigma = 0.01$, Eq. (1) was the only one of the investigated models that gave a straight-line dependence. Thus, with such a noise level, the determina-

Table 1

Estimated values of rate constants, $k_i \cdot 10^{-3}$ (σ=0.01)

T, K	Type I, n=2/3	Literature data
854	19.5±0.5	19.8
833	10.9±0.2	11.0
820	7.44±0.06	7.45
814	7.29±0.06	7.25
805	4.80±0.06	4.86
800	4.16±0.03	4.15
795	3.67±0.03	3.64

tion of the correct model could be made at as early as the first stage of analysis, during linearity tests. The calculated rate constants (Table 1), activation energies and pre-exponential factors (Table 2) fitted the literature data well. It should be noted, however, that most experimental work involves much larger uncertainties though, in principle, current techniques allow the attainment of rather low reproducibility errors.

The situation with $\sigma = 0.1$ is the most typical one. In addition to the starting model (1), three type I models ($n = 2/3$, 1/2 and 1/3) and one type III model ($m = 1$) were selected in this case. All these models were applied to calculation of the rate constants k_i corresponding to the chosen temperature points (Table 3). The values obtained varied widely from one model to another. The type III model gave constants markedly different from those cited in the literature, and only the type I model with $n = 2/3$ yielded values consistent with the experimental ones. The fact that different models lead to different rate constants has already been mentioned [4]. However, this suggestion has been made on the basis of intuitive considerations, without analysis of effects by experimental errors.

We conclude that unambiguous choice of the mathematical model in the case of $\sigma = 0.1$ is possible provided a single experimental k_i value is known.

Table 2

Estimated values of kinetic parameters*

		Type I			Type III	Literature data
		n=1/3	n=1/2	n=2/3	m=1	
σ=0.01	E	–	–	39±2	–	39±2
	ln A	–	–	19±1	–	19±1
σ=0.1	E	35±7	33±5	40±4	36±6	39±2
	ln A	17±5	15±3	20±2	18±3	19±1

* Values of ln A and E/R give a correlation of about 0.99.

The ultimate aim of any kinetic study is the determination of kinetic parameters describing the process. We have evaluated activation energies E and pre-exponential factors A from the values of rate constants k_i obtained for the three models described above. Table 3 compares estimates based on various models.

Table 3

Estimated values of rate constants, $k_i \cdot 10^{-3}$ (σ=0.1)

$T°$, K	Type I			Type III $m=1$	Literature data
	$n=1/3$	$n=1/2$	$n=2/3$		
854	–	–	20.1±2	70±10	19.8
833	–	14 ±0.9	10.6±0.7	40±5	11.0
820	11.6±0.7	9.8±0.6	7.3±0.5	25±4	7.4
815	11.4±0.6	9.5±0.6	7.1±0.5	24±4	7.2
805	8.2±0.6	6.6±0.5	4.7±0.3	15±2	4.9
800	7.3±0.3	6.0±0.5	4.5±0.3	14±1	4.2
795	6.4±0.3	5.4±0.3	3.9±0.3	11.0±0.9	3.6

It should be noted that the Arrhenius equation

$$\ln k = \ln A - \frac{E}{R} \cdot \frac{1}{T}$$

which belongs to the $y = a + bx$ type of linear equations, with a for $\ln A$, b for E/R, y for $\ln k_i$, and x for $1/T$, always involves a strong correlation between the parameters. The correlation was often as high as about 0.9 in our case. Hence two-dimensional normal distribution should be applied in order to determine the significance of the divergence in the parameters obtained from different models. This was done by using the Hotteling criterion T^2. The calculated T^2 values are presented in Table 4. Only model (1) was found to yield parameter values in agreement with the literature data.

Table 4

T^2-criterion values obtained by comparison of kinetic parameters for models selected at σ=0.1 ($T^2_{theor} = 4$)

	Erofeev equation	$n=1/3$	$n=1/2$	$n=2/3$	Literature data
Erofeev equation		0.6	5.2	5.2	9.1
$n=1/3$			2.5	4.3	5.2
$n=1/2$				23	14
$n=2/3$					3.6

The results of this investigation show that the models that can not be applied to the process in question give equivalent sets of parameters which are different from the literature data and from the parameters predicted by model (1). It follows that the comparison of the corresponding parameters may provide indirect evidence in favour of the right model. The statistical method suggested in this work should be applied in order that the significance of the differences between the parameters predicted by different models or obtained for different processes might be established. The utility of this approach depends on a strong correlation between the Arrhenius parameters. A comparison of isolated parameter values with the 2σ values leads to erroneous conclusions.

The results of this investigation are as follows. Analysis of the experimental data leads to different results depending on the reproducibility errors. The statistical approach applied allows one to determine the input mechanism unambiguously when σ has the value of 0.01. With $\sigma = 0.1$, which is a more frequent situation, the choice of the model can only be made on the basis of a detailed statistical analysis and comparison of the results obtained with the literature data. With the larger reproducibility errors, it is impossible to make a definite conclusion about the reaction mechanism.

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RÉSUMÉ — On considère un processus modèle pour vérifier s'il est possible d'appliquer une approximation statistique particulière pour déterminer le mécanisme initial des réactions topochimiques et le modèle mathématique respectif.

On montre que l'analyse des données expérimentales conduit à des résultats différents en raison des erreurs de reproductibilité. L'application de cette approximation statistique permet de déterminer le mécanisme initial sans équivoque, pourvu que la valeur de σ soit égale à 0.01.

ZUSAMMENFASSUNG — Ein Modellverfahren wird zur Untersuchung der Anwendbarkeit einer bestimmten statistischen Näherung zur Bestimmung eines Inputmechanismus topochemischer Reaktionen und des einschlägigen mathematischen Modells herangezogen.

Es wird gezeigt, daß infolge von Reproduzierbarkeitsfehlern die Analyse der Versuchsangaben zu verschiedenen Ergebnissen führt. Die angewandte statistische Annäherung gestattet die eindeutige Bestimmung des Inputmechanismus bei einem Sigma-Wert von 0.01.

Резюме — Рассмотрен модельный процесс для исследования применимости частного статистического приближения к определению какого-либо входного механизма топохимических реакций и соответствующей математической модели. Показано, что анализ экспериментальных данных приводит к различным результатам, что обусловлено ошибками воспроизводимости. Примененное статистическое приближение позволяет однозначно определить входной механизм, когда σ имеет значение 0,01.