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 $\sigma$ 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: $\text{ZnO} + \text{H}_2 = \text{Zn} + \text{H}_2\text{O}$, 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:

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

(1)

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For comparison, the following equations were chosen:

- type I: \(1 - (1 - \alpha)^{1-n} = kt\) where \(n = 0, 1/2, 2/3, 3/4\) (2)
- type II: \(\ln \frac{\alpha}{1 - \alpha} = kt + C\) (3)
- type III: \(\alpha = 1 - e^{-k't^m}\) where \(m = 1, 2, 3, 1/2, 3/4\) (4)

Here \(\alpha\) 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

\[k = n(k')^{1/n} (k = m(k')^{1/m})\]

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 \(\alpha_i\) 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 \(\alpha_i\) values using the random numbers table and \(\sigma \) 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-