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SOME ASPECTS OF MATHEMATICAL STATISTICS AS APPLIED TO NONISOTHERMAL KINETICS V.

Comparison of the Amount of Information Obtained in Traditional and Nontraditional Approaches

S. V. Vyazovkin and *A. I. Lesnikovich*

INSTITUTE OF PHYSICO-CHEMICAL PROBLEMS, MINSK, USSR

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The paper gives a quantitative comparison of two methodological approaches to the solution of the inverse kinetic problem: the traditional approach and the nontraditional approach suggested by the authors. It is shown that the amount of information (in the sense of Shannon) obtained within the scope of the nontraditional approach is always greater than that obtained with the use of the traditional approach.

In the previous Part [1] considering the methodological aspects of a formal description of heterogeneous processes, two approaches to the ambiguous solution of the inverse kinetic problem, traditional and nontraditional, were emphasized. The former is based on the principle of an unambiguous description; the latter relies on the principle of complementarity. The salient feature of the nontraditional approach is the simultaneous application of several kinetic functions to describe the process, which allows a description yielding more information. The present work seeks to give a quantitative estimation of the merits of the nontraditional methodology, as far as the information obtained is concerned, in solving the inverse kinetic problem.

According to Lindley [2], the information obtained in the experiment corresponds to the variations of the entropy of a posteriori distribution $H(p^*)$ as against the entropy of a priori distribution $H(p^\circ)$:

$$I = H(p^\circ) - H(p^*) \tag{1}$$

The entropy of a discrete distribution is estimated through the Shannon formula [3] as

$$H(p) = -\sum_{i=1}^{L} p_i \log p_i \tag{2}$$

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where p_i is the probability of the i-th event. As the experimental data produce information only within the scope of the appropriate models [4], we shall give some elucidation concerning the models and information under consideration.

Any quantitative method of interpreting the experimental data generates its own probability distributions. The method of solution of the inverse problem is no exception in this sense. As concerns our classification into traditional and nontraditional methods of solution of the inverse kinetic problem [1], two appropriate solution models may be singled out. Mathematically, they differ in generating different kinds of a posteriori distribution p^*, which will be shown below. It should be noted that the information produced by these models is that obtained from the selection of the kinetic functions used to describe the experimental data. The principle of selection is determined by the model of solution of the inverse kinetic problem, i.e. by the methodology used.

A set of about twenty kinetic functions is usually employed to describe heterogeneous processes. Then, in terms of (1), the i-th event is the description of the experimental data by the i-th kinetic function; p_i is the description probability for the i-th function; L is the number of functions used for the description. In the case when there is no a priori information on the process corresponding to some kinetic function, all of them are equally probable, which is consistent with uniform a priori distribution p° (Fig. 1). The entropy of a uniform distribution in formula (2) is

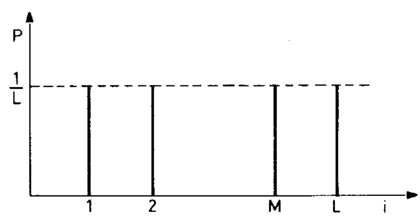

Fig. 1 A priori distribution of process description probability by means of α kinetic functions

$\log L$. Following the experiment, the results will probably be described by different kinetic functions with different probabilities, which is consistent with some a posteriori distribution p^* (Fig. 2), where p_m is the maximum probability.

Let us compare the amount of information extracted from the thermoanalytical experiment, using traditional and nontraditional methodologies [1] in order to solve the inverse kinetic problem. The nontraditional methodology, based on the principle of complementarity, allows the entire set of kinetic functions to be used for the description of the process, and relies on the distribution shown in Fig. 2. Therefore, the amount of information extracted from the experimental data will be

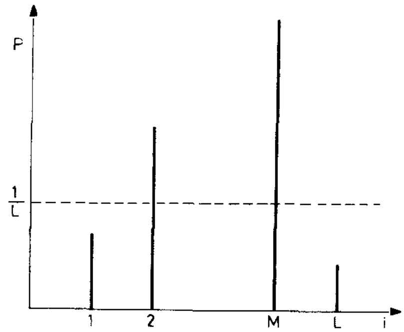

Fig. 2 A posteriori probability distribution in the case of nontraditional model

in accordance with formula (1):

$$I = \log L + \sum_{i=1}^{L} p_i \log p_i \tag{3}$$

The traditional methodology, based on the principle of an unambiguous description, allows the use of the unique and most probable kinetic function, i.e. the one corresponding to the maximum correlation coefficient or the minimum residual sum of squares. In this case, the functions with probabilities below p_m are omitted and, hence, the information corresponding to these functions is ignored in the explicit form. This does not mean, however, that it is zero. Evidently, all the omitted $L-1$ functions seem to be equally unsuitable to describe the experimental data, i.e. they are equi-probable. The a posteriori distribution in this case will therefore assume the form shown in Fig. 3. The amount of information derived within the scope of the traditional model of the inverse kinetic problem solution will be (Fig. 3)

$$I_T = \log L + \bar{P}_m \log p_m + (1-\bar{P}_m) \log \frac{1-\bar{\bar{P}}_m}{L-1} \tag{4}$$

To compare (3) and (4), we rewrite (3) as

$$I = \log L + p_m \log \bar{\bar{P}}_m + \sum_{i=1 \neq m}^{L} \bar{\bar{P}}_i^* \log \bar{\bar{P}}_i^* \tag{5}$$

The last term in (5) is the entropy of opposite sign. The entropy is known to be maximum when all p_i are equal [4], i.e.

$$\mathrm{MAX}\left(-\sum_{i=1 \neq m}^{L} \bar{\bar{P}}_i^* \log \bar{\bar{P}}_i^*\right) = -(1-\bar{P}_m) \log \frac{1-\bar{\bar{P}}_m}{L-1} \tag{6}$$

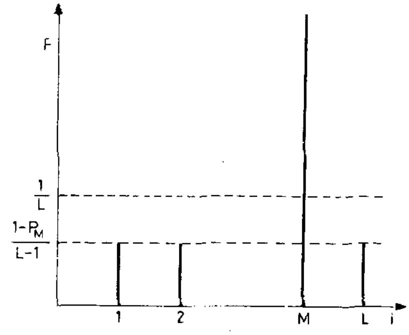

Fig. 3 A posteriori probability distribution in the case of traditional model

or

$$\mathrm{MIN}\,(\sum_{i=1/m}^{L} \bar{\bar{P}}_i^* \log \bar{\bar{P}}_i^*) = (1-\bar{\bar{P}}_m)\log\frac{1-\bar{\bar{P}}_m}{L-1} \tag{7}$$

In view of (7), it follows from a comparison of (4) and (5) that

$$I > I_T \tag{8}$$

i.e. the nontraditional model of solution of the inverse kinetic problem is more informative than the traditional one.

Calculation of the description probability

The probability of description of the experimental data by the i-th kinetic function was calculated in the following way. Residual dispersions were estimated with the use of the least-squares method for each L kinetic function substituted into the Coats–Redfern equation [6]. Thus, L residual dispersions were obtained, their ratio obeying the Fisher distribution law [7]. When the number of degrees of freedom ν is equal for all residual dispersions, the Fisher distribution is of the form

$$\bar{\bar{P}} = \frac{1}{B\left(\frac{\nu}{2},\frac{\nu}{2}\right)} \int_0^F X^{\frac{\nu}{2}-1}(1+x)^{-\nu}\,dx \tag{9}$$

where B is the beta-function [8] and F is determined by the greater-to-smaller dispersion ratio. Then, p is the probability for the greater dispersion to exceed the smaller one.

With the use of the available set of L dispersions, the ratios

$$F_i = \frac{S_i^2}{S_{\min}^2} \tag{10}$$

where $S_{\min}^2$ is the minimum dispersion of all S_i^2, were calculated and substituted into (9). The probability of experimental data description by the i-th kinetic function was taken to be proportional to $1-\bar{\bar{P}}$, i.e. to the probability that this kinetic function gives a (statistically) better description than the function corresponding to $S_{\min}^2$. Final probabilities were calculated on the assumption that the experimental data with L kinetic functions are described by a complete and independent system of events, i.e.

$$\sum_{i=1}^{L} \bar{\bar{P}}_i = 1 \tag{11}$$

The results of calculation with the experimental data for the decomposition of two magnesium hydroxide samples [9] (Table 1) exemplify the above method. Nineteen kinetic functions were used in the calculations. The tabulated probability values are rounded off to 4 decimal places. Eleven kinetic functions, omitted from Table 1, have probability of less than 10^{-4}. It is seen from Table 1 that the amount of information derived within the scope of the nontraditional model of solution of the inverse kinetic problem is, on the average, 1.26 times that for the traditional model. This amount constitutes 80 percent of the maximum possible information, while the traditional model yields 63 percent.

Table 1 The description probability values for the different kinetic functions

Kinetic functions		Probability	
		trace 1	trace 2
$\alpha^{1/4}$		0.0107	0.0235
$\alpha^{1/3}$		0.0003	0.0008
$(-\ln(1-\alpha))^{1/4}$		0.7946	0.7876
$(-\ln(1-\alpha))^{1/3}$		0.1852	0.1819
$(-\ln(1-\alpha))^{1/2}$		0.0040	0.0038
$(-\ln(1-\alpha))^{1/1.5}$		0.0001	0.0001
$(1-\alpha)^{-1/2}-1$		0.0024	0.0002
$(1-\alpha)^{-1}-1$		0.0027	0.0021
Quantity of information (bit)	I	3.38	3.34
	I_T	2.66	2.67

Conclusion

It is shown that the selection of functions within the scope of the nontraditional methodology gives more comprehensive primary information as compared with the choice of one (best) function in accordance with the traditional methodology. As concerns further extraction of information from experimental data, this implies the estimation of kinetic parameters using the chosen kinetic functions and appropriate confidence limits. In this case, the amount of information may also be determined by formulas (1) and (2). However, the model generated by a posteriori distribution in (1) will be represented by a particular kinetic function, and the probabilities in formula (2) will be related to the experimental values on the kinetic curve.

It is evident that in this case too a greater amount of information will be obtained within the scope of the nontraditional methodology, since the latter involves the information corresponding not only to the most informative kinetic function, but also to all others.

The informative merits of the nontraditional methodology of solution of the inverse kinetic problem make it possible to increase the accuracy of estimation of the kinetic parameters. This follows from the inverse proportion between the bulk of information used to determine the parameters and the volume of the confidence region for them [10].

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Zusammenfassung — Zwei methodologische Näherungen der Lösung des inversen kinetischen Problems werden quantitativ verglichen, nämlich die traditionelle und die von den Autoren vorgeschlagene nicht-traditionelle Näherung. Es wird gezeigt, daß mit der nicht-traditionellen Näherung erhaltene (im Sinne von Shannon verstandene) Informationsmenge immer größer als die durch Anwendung der traditionellen Näherung erhaltene ist.

Резюме — В работе дано количественное сопоставление двух методологических подходов к решению обратной кинетической задачи: традиционного и предложенного авторами нетрадиционного. Показано, что количество информации (в смысле Шеннона), получаемой в рамках нетрадиционного подхода, всегда больше, чем при использовании традиционного подхода.