

SOME ASPECTS OF MATHEMATICAL STATISTICS AS APPLIED TO NONISOTHERMAL KINETICS

Part III. Unified approach to the analysis of kinetic functions

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(Received March 4, 1986)

The suggested unified approach is based on the consideration of the entire set of kinetic functions as some space. The analysis of this space provides four classes of kinetic functions, characterized by similar properties and close values of kinetic parameters. The solution of the inverse kinetic problem within the unified approach reduces to finding unambiguously the class of kinetic functions.

A wide set of diverse kinetic functions is used, as a rule, to solve the inverse kinetic problem. The diversity of kinetic functions concerns both their physical meaning and the mathematical form for its expression. The absence of a uniform approach to describe the whole set of kinetic functions prohibits their objective choice for the description of particular processes in solid substances. Therefore, investigators often restrict their consideration to some class of kinetic functions containing the adjustable parameter (functions of the Avrami–Erofeev type, of the reaction order). Their main advantage consists in permitting study of the formal process characteristics (E and $\log A$), continuously changing as a function of the adjustable parameter. In this case the characteristics underlying the choice of the function giving the finest description of the process (correlation coefficient, residual sum of squares) change continuously. The shortcoming in describing the process by kinetic functions of one class is that the real ‘best’ kinetic function may enter another class. Further, there are some kinetic functions which do not contain the adjustable parameter (functions of diffusion processes, Mampel and Prout–Tompkins functions).

The function may be chosen by sorting all possible kinetic functions, but it would be more reasonable to do this through the unified approach. By the unified approach, we understand a technique which would allow one to consider the kinetic functions by analysing their mathematical form rather than elaborating their

physical meaning. Such an approach is quite admissible, as the kinetic functions in their essence are formalized descriptions of idealized chemical processes. It is clear that the possibility of combining any kinetic functions in a single system should be an integral property of the unified approach. This property will always be inherent to the space formed by the kinetic functions, irrespective of their number and form.

This paper considers kinetic functions within the suggested unified approach, as well as its application to the solution of the inverse kinetic problem in the framework of nonisothermal kinetics. Mathematically, this requires finding a characteristic of the entire space of kinetic functions which may play the same role as the adjustable parameter does for some of their classes.

The space of kinetic functions

Let us consider some space containing all kinetic functions. Evidently, the dimension of a space determined by the number of orthogonal kinetic functions is much less than the number of all possible functions. In particular, the compensation effect (imaginary) or, in other words, the multicollinearity of the kinetic functions indicates this fact.

We shall now introduce in this space the operation of the scalar product [1]:

$$c_{ij} = \int_{\alpha_1}^{\alpha_2} f_i(\alpha) f_j(\alpha) d\alpha \quad (1)$$

where $f_i(\alpha)$ and $f_j(\alpha)$ are different kinetic functions, while α_1 and α_2 are the initial and final degrees of decomposition.

In the case the $i = j$, we obtain the norm of kinetic function $f_i(\alpha)$:

$$c_i = \left(\int_{\alpha_1}^{\alpha_2} (f_i(\alpha))^2 d\alpha \right)^{0.5} \quad (2)$$

Taking account of (1) and (2), the angle between the kinetic functions may be estimated as:

$$\cos \theta_{ij} = \frac{c_{ij}}{c_i c_j} \quad (3)$$

Quantity (3) is a fundamental characteristic of the space of kinetic functions, since it determines the relationship between them. Its value ranges from 0 to 1, which corresponds to the change of the ratio of functions from absolute independence to perfect equivalence. This is the fundamental character of this quantity, which served as the basis to construct the required adjustable parameter.

Below we shall consider a particular form of this parameter and its possible application to solution of the inverse kinetic problem.

The space of kinetic functions of the reaction order type

Since the kinetic functions of this class have the adjustable parameter, consideration of this space within the unified approach is of purely methodological importance.

The values of (3) were calculated for this space using both differential $f(\alpha)$ and the integral $g(\alpha)$ forms of the kinetic functions. In calculating (1) and (2), it was assumed that $\alpha_1 = 0.01$ and $\alpha_2 = 0.5$ and 0.9 . The value of the reaction order n varied from 0 to 2. The results are listed accordingly in Tables 1 and 2 for the differential and integral forms of the kinetic functions.

Table 1 Values of angles θ between kinetic functions $f(\alpha) = (I - \alpha)^n$ vs n and α_2

n	α_2				
0	0.5				
	0.9				
0.5	0.5	5.5			
	0.9	14.7			
1.0	0.5	10.8	5.3		
	0.9	25.2	10.8		
1.5	0.5	15.7	10.2	5.0	
	0.9	32.8	18.8	8.1	
2.0	0.5	20.2	14.8	9.5	4.6
	0.9	38.3	24.8	14.4	6.4
	α_2				
	n	0	0.5	1.0	1.5

The main conclusions of the analysis of this space (Tables 1 and 2), which also seem to be valid for other spaces of kinetic functions, are as follows:

- (i) increase of the interval $\alpha_1 - \alpha_2$ leads to an increasing angle between the kinetic functions;
- (ii) the differential forms of the kinetic functions yield high values of the angles as compared to the integral ones.

These conclusions may serve as a methodological basis to improve the conditionality of inverse kinetic problems. Evidently, the greater the angle between the functions, the greater the difference between them and the simpler their discrimination is. Thus, in the case of a formal kinetic analysis of the process it is preferable to use wider intervals of the degrees of decomposition and the differential methods to estimate the kinetic parameters.

Table 2 Values of angles θ between kinetic functions

$$g(\alpha) = \frac{I - (I - \alpha)^{I-n}}{I-n} \text{ vs } n \text{ and } \alpha_2$$

n	α_2				
0	0.5				
	0.9				
0.5	0.5	1.8			
	0.9	4.5			
1.0	0.5	3.8	2.0		
	0.9	11.2	6.8		
1.5	0.5	5.9	4.1	2.0	
	0.9	19.6	14.7	8.3	
2.0	0.5	8.1	6.2	4.3	2.1
	0.9	28.3	23.4	16.8	8.9
	α_2 / n	0	0.5	1.0	1.5

The space being two-dimensional is one more important property. This statement can easily be verified, as for any three kinetic functions the sum of the angles formed by one function with the other two is equal to the angle between the extreme functions.

Taking any function of this space as a basis, we may write, by virtue of the two-dimensional character:

$$f_i(\alpha) \approx f_0(\alpha) \cos \theta_i \quad (4)$$

where $f_0(\alpha)$ is the basic kinetic function, and θ_i is the angle between functions $f_i(\alpha)$ and $f_0(\alpha)$.

With regard to (4), the main nonisothermal kinetic equation will assume the form:

$$\frac{d\alpha}{dT} \approx \frac{A}{q} \exp\left(-\frac{E}{RT}\right) f_0(\alpha) \cos \theta_i \quad (5)$$

From the statistical point of view, the solution to the inverse kinetic problem using linearized form (5) reduces to the search of a minimum residual sum of squares (6):

$$s^2 \approx \sum_{j=1}^k \left(\ln \frac{d\alpha_j}{dT_j} - \ln (f_0(\alpha_j)) - \ln (\cos \theta_i) - \ln \frac{A_i}{q} + \frac{E_i}{RT_i} \right)^2 \quad (6)$$

The mathematical form of Eq. (6) shows that the s^2 dependence on $\ln(\cos \theta_i)$ is expressed by some convex function. The particular form of the extreme is stipulated by the existence of a solution to the corresponding normal equation (7), stemming from (6):

$$\frac{\partial s^2}{\partial \ln(\cos \theta)} = 0 \quad (7)$$

(iii) If the solution to (7) in the prescribed θ interval does exist, the s^2 dependence on $\ln(\cos \theta_i)$ will have a minimum. If it does not, the dependence has a maximum.

This is the third methodological conclusion which follows from the analysis of the two-dimensional space of reaction orders, and it is of special importance to analyse the space of kinetic functions of more complex structure. Further, Eq. (6) yields a particular form of a sought adjustable parameter ($\ln(\cos \theta)$) that may be applied to analyse any two-dimensional space. This property of the adjustable parameter enables one to develop a unified approach to the analysis of the entire space of kinetic functions as a set of some two-dimensional subspaces.

Entire space of kinetic functions

The considered entire space of kinetic functions contains 20 functions taken from [2]. The fact that such a space is indeed entire will become understandable from what follows. The values of (1) and (2) were calculated using the Simpson method [1] at $\alpha_1 = 0.01$ and $\alpha_2 = 0.9$. The results are given in Table 3.

Analysis of the angles formed by the kinetic functions provides four classes of functions in the entire space under consideration, each of the classes being a two-dimensional subspace.

1. The class of diffusion kinetic functions includes functions Nos 13 to 16. It is worth noting that the analysis assigns function No. 6 to this class, as it stands much closer to the diffusion functions than to the functions for the power law of nuclear growth.

2. The class of kinetic functions of the general form $(1-\alpha)^p$ includes the functions of the Mampel type (No. 7), the contracting sphere (No. 19), and the contracting cylinder (No. 20). They also cover all the kinetic functions of the reaction order.

3. The class of kinetic functions of the Avrami-Erofeev type includes functions Nos 8 to 11 and the Prout-Tompkins function No. 12.

4. The class of kinetic functions of the general form $m\alpha^n$ comprises the power-law nuclear growth functions Nos 1 to 3, and also the exponential law oxidation functions Nos 17 and 18, which are completely equivalent within the unified approach.

Some functions, however, are intermediate between the above classes. For instance, the power-law growth function No. 4 is between classes 4 and 3, and function No. 5 between classes 1 and 3.

The division of the entire space of kinetic functions into four sub-spaces or, in other words, combining the considered set of kinetic functions into four classes relies upon the formal form of the functions, which can easily be seen from a comparison of the functions of one class. The close values of the kinetic parameters and residual sums of squares obtained for the kinetic functions of one class indicate that such a combination is not arbitrary. Further, the dependences of the type $E - \ln(\cos \theta)$ and $\log A - \ln(\cos \theta)$ provide the compensation effects, which are different for each of the classes. Figure 1 shows the compensation effects for different classes of functions obtained by interpreting the model data $\left(T, \alpha, \frac{d\alpha}{dT}\right)$ for the function $(1 - \alpha)^{1.5}$ at $E = 30$ kcal/mol, $\log A = 15$. In addition to the above 20 functions, they include two functions with reaction order $n = 2.0$ and $n = 1.5$.

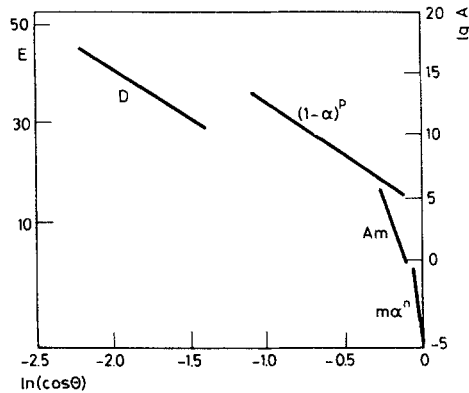


Fig. 1 Compensation effects of types $E - \ln(\cos \theta)$ and $\log A - \ln(\cos \theta)$ for different classes of kinetic functions

Conclusion (iii) is supported by the dependence $s^2 - \ln(\cos \theta)$ for the same model data in Fig. 2. It can easily be seen that the minimum here appears only for the class of kinetic functions of the general form $(1 - \alpha)^p$. As concerns the other classes, they can be ignored in this case, as the appropriate dependences $s^2 - \ln(\cos \theta)$ have no minima at all. It should be noted that the values of $\ln(\cos \theta)$ will be obtained with regard to the angles formed by each of the kinetic functions and the one giving minimum kinetic parameters. Otherwise, the corresponding dependences will have a fracture.

As concerns the question of how complete the space of kinetic functions is, the

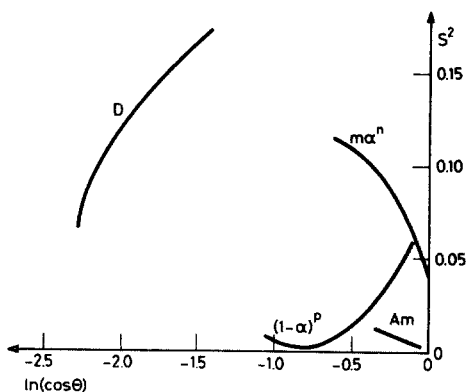


Fig. 2 Dependence s^2 on $\ln(\cos\theta)$ for different classes of kinetic functions

“discontinuity” between the class of diffusion kinetic functions and the functions $(1-\alpha)^p$ in Figs 1 and 2 may be eliminated by increasing p . Hence, the above four classes embrace all possible kinetic functions.

Unified approach as applied to solution of the inverse kinetic problem

It has already been seen that the suggested unified approach enables one to choose the class of kinetic functions containing the one which gives the best description of the process. In addition to the model data for the function $(1-\alpha)^{1.5}$, the model data for the kinetic functions of other classes were considered. In all cases, the classes including the “best” kinetic function were appropriately found by analysing the form and interposition of s^2 vs $\ln(\cos\theta)$. Analysis of the data [3] using the suggested approach allows the class of kinetic functions $(1-\alpha)^p$ to be chosen unambiguously. The authors [3] have also chosen the function of the reaction order entering this class. Their choice, however, based on the application of several calculation procedures pointing to the function of the reaction order as one of the best, is not strictly based statistically, as the significance of the difference between the “best” and other functions was not estimated. In this case, the reaction order function competed with the Avrami–Erofeev functions representing an individual class within the suggested unified approach, thereby stipulating, finally, the unambiguous choice of the class of $(1-\alpha)^p$ functions.

Accordingly, in the solution of the inverse kinetic problem, the unified approach allows one to avoid ambiguity in choosing a class of kinetic functions. As concerns ambiguity due to the choice of a function inside some class, it does not disappear, as

inevitably follows from the experimental errors. In the case of the unified approach applied, such an ambiguity inside a class can easily be interpreted as due to experimental errors in the kinetic parameters. The latter can be determined by considering s^2 vs E and s^2 vs $\log A$ for the chosen class of kinetic functions. It is known that such dependences are represented by convex downward functions. The values of the kinetic parameters are therefore taken as their mathematical expectation. The confidence intervals of the kinetic parameters can be constructed by taking account of the Fischer distribution. To avoid intricate calculations, s^2 vs E and s^2 vs $\log A$ must be approximated with polynomials.

If the chosen class of kinetic functions contains the adjustable parameter, its value corresponding to the minimum may be given and its confidence intervals may be estimated by analogy with the kinetic parameters. If it does not, then the kinetic function giving the value of s^2 closest to the minimum may be regarded as an estimator.

Conclusion

1. The suggested approach for analysing kinetic functions provided their combination in four classes. The combining of kinetic functions in one class on the basis of a formal criterion may be explained hypothetically in two ways. First, it may be due to some imperfect kinetic functions (the mathematical form being inadequate for the physical content of the real process). It is evident that in this case inspection and change of the mathematical form in order to bring it into agreement with the physical content will provide a more correct and detailed classification of the processes under consideration. Secondly, it may point to some objective community of the analysed processes (the mathematical form being adequate for the physical content), which is not revealed either theoretically or experimentally yet. Hence, the studies in this direction must be of considerable interest.

2. The suggested approach provides a new means of solving the inverse kinetic problem, by choosing a class rather than a function. The advantage lies in the unambiguity of the choice. In this case, the ambiguity appearing in the choice of a function inside a class is interpreted as an error in the kinetic parameters, which follows logically from the unity of the processes in one class.

References

- 1 G. A. Korn and T. M. Korn, *Mathematical Handbook for Scientists and Engineers*, McGraw-Hill, 1968.
- 2 P. V. Ravindran, T. P. Radhakrishnan and A. K. Sundaram, *Government India Atom. Energy Commis.*, No. 927, 1977.
- 3 P. H. Fong and D. T. Y. Chen, *Thermochim. Acta*, 18 (1977) 273.

Zusammenfassung — Die vorgeschlagene vereinheitlichte Näherung geht davon aus, daß das gesamte System der kinetischen Gleichungen als Raum angesehen wird. Die Analyse dieses Raumes ergibt vier Klassen von kinetischen Funktionen, die durch ähnliche Eigenschaften und geschlossene Werte der kinetischen Parameter charakterisiert sind. Die Lösung des inversen kinetischen Problems reduziert sich in der vereinheitlichten Näherung auf das eindeutige Auffinden der Klasse der kinetischen Funktionen.

Резюме — Предлагаемый единый подход основан на рассмотрении всей совокупности кинетических функций как некоторого пространства. Анализ данного пространства позволяет объединить кинетические функции в четыре класса, характеризующихся близостью свойств и значений кинетических параметров, причем решение обратной кинетической задачи сводится к нахождению класса кинетических функций, которое осуществляется однозначно.