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A METHOD OF FINDING INVARIANT VALUES OF KINETIC PARAMETERS

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A method of calculating the Arrhenius parameters has been proposed, based on an evaluation of the coordinates of intersection of greatly extended confidence regions determined in solving the inverse kinetic problem. The validity of this method is illustrated by comparison of the Arrhenius parameters found from non-isothermal and isothermal data reported by other investigators.

The kinetic parameters characterizing the chemical stage of solid-phase reactions are determined by isothermal kinetic methods, provided certain approaches to the selection of a theoretical model are observed and rigid constraints are imposed on the experiment [1]. Such constraints may yield a positive result in non-isothermal kinetics [2] as well. However, finding the kinetic parameters from experimental data, i.e. solving an invers kinetic problem, may run into certain difficulties, for such problems are ill-posed mathematical problems characterized by a poor statement of the problem conditions (the determinant of the information matrix is close to zero). Therefore, such problems have no unique solution unless special methods are used [3]. This problem was analyzed in [4, 5] for dynamic thermogravimetry conditions. The poor statement of the problem conditions determines its solution in the form of a greatly extended region, so that experimental data can be described with equal accuracy with the help of Arrhenius parameters A and E variable over a very wide range in this region, the compensative effect being an artefact of computation. Calculated by different methods, A and E characterize the mathematical method used rather than the reaction itself. This also follows from [6–9]. The artefact can be eliminated, partially at least, by transforming the Arrhenius equation with the help of new variables ($T^{+} = \frac{T-\bar{T}}{T}$ and others, where $\bar{T}$ is the mean or harmonic temperature [3, 10, 11]. The invariant characteristics of the process can also be calculated with a different, quite general means, by constructing a statistical model of the process as a polynomial [3]. In this paper a method is suggested for determining invariant values of the activation energy (E) and a pre-exponential factor (A), which corresponds to the above general approach. Isokinetic temperature and a polynomial as a polylinear expansion [12] are used in the method. This makes it very simple to use in computation and provides a very clear interpretation that reveals the physical meaning of the invariants obtained. The essence of the method is described in [13], where a possibility is shown to determine invariant values of the activation energy and the pre-exponential factor by an example of kinetic data applied to heterogeneous catalytic reactions. This determination is based on the use of a kinetic compensative effect, which is known to be the condition of forming a pencil by the Arrhenius lines for the Arrhenius equation. Certain variations of the experimental conditions lead to several such pencils, whose centres lie on one straight line. It follows from simple geometric considerations that this straight line specifies the values of E and A. The latter are invariant under rather diverse experimental conditions and can be considered as "true" kinetic parameters.

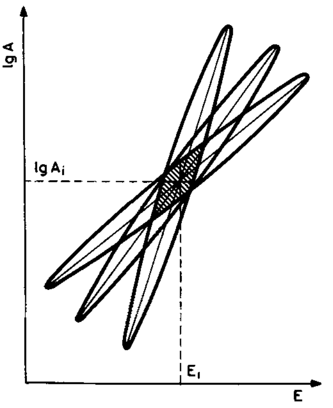

Fig. 1 A schematic plot of the intersection of the confidence regions when condition (2) is valid

In order to explain the essence of the method, we consider Fig. 1. The Figure illustrates schematically the confidence regions for three relationships of the type

$$\log A = B + eE \qquad (1)$$

each of which is associated with great ambiguity in the determination of A and E. If varying the experimental conditions yields a set of relationships (1) with linearly dependent parameters B and e, then straight lines (1) form a pencil whose centre coordinates give the desired $\log A_i$ and E_i whith some error (cross in Fig. 1). To be more precise, it is the corresponding confidence regions rather than the idealized straight lines (1) that intersect. The intersection of these regions determines a smaller size of the total confidence region (common to all the initial ones), which is shown in Fig. 1 as a hatched area. Thus, a sharp decrease of uncertainty in the values of A and E becomes obvious.

The main problem of practical application of the suggested method is whether the set of relationships (1) with the correlating parameters B and e exists. On the basis of vast experimental material on heterogeneous catalysis obtained by many authors, in

[13] the existence of such sets is shown, which is manifested by the validity of the "supercorrelation"

$$B = f - ge \tag{2}$$

which is the Arrhenius equation for the coordinates of the centre of pencils arising from the Arrhenius straight lines according to (1).

In the region of non-isothermal kinetics, the validity of (2) is also confirmed by the experimental data of [14] on the kinetics of calcium oxalate dehydration studied by isothermal and non-isothermal methods. The first of these methods was used to find the A and E values invariant with respect to the changes of some experimental conditions and calculation methods. These values range from 10.84 to 11.33 s^{-1} for $\log A$ and 27.95 to 28.57 kcal mol^{-1} for E. The non-isothermal experiments with variations of the heating rate and the theoretical model for the fraction conversion function $F(\alpha)$ have revealed much wider ranges of the obtained $\log A$ and E: 40.0 to 0.127 and 86.1 to 5.08, respectively. Even after $F(\alpha)$ had been chosen on the basis of isothermal experiments, these ranges were 16.94 to 3.93 and 40.04 to 12.66.

Non-isothermal kinetic data do not practically permit us to give preference to any function $F(\alpha)$ over the 12 functions tested in [14], since a high correlation coefficient (from 0.9705 to 0.9998) corresponds to each of the function. Therefore, in accordance with the suggested method, we have found a value of the rate constant (K_i) invariant with respect to $F(\alpha)$ at isokinetic temperature (T_i) for every heating rate used in [14]. Actually, we have obtained concrete relations (1), i.e. $e = 1/2.3RT_i$ and $E = \log K_i$. Further, if the process mechanism does not change with the heating rate, then the Arrhenius relation may be expected to hold between K_i and T_i, i.e. (2) is satisfied and may be used to find A_i and E_i invariant with respect to the heating rate, since $f = \log A_i$, and $g = E_i$. Figure 2 illustrates the validity of (2). In this Figure, $\log A_i = 11 \pm 2$ and $E_i = 26 \pm 5$. The point for the heating rate of 4.71° min^{-1} is somewhat outside the permissible errors. With this point neglected, $\log A_i = 11 \pm 1$ and $E_i = 28 \pm 3$. The values of A and E actually coincide with those obtained with the isothermal data; however, the errors in A and E are greater. They

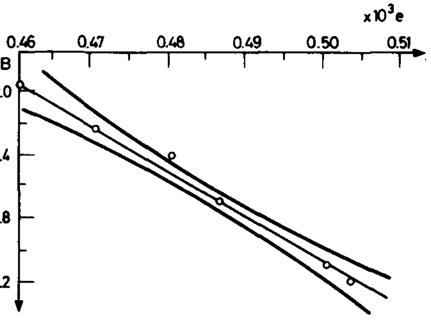

Fig. 2 The dependence of B on e, determined by treating data [14]

are, however, much smaller than the range of uncertainty for $\log A_i$ and E_i obtained by the non-isothermal method, even after $F(\alpha)$ is selected on the basis of the isothermal data.

Other examples of the validity of (2) in non-isothermal kinetics can also be given. Hence from the data of [15], obtained for a number of related cobalt complexes, one may get (2), with one point falling out.

If the nature of the related compounds varies, the compensative effect can be classified as a true one [16]. Therefore, the meaning of the correlation (2) will be different. It probably reflects the invariant stage in the complicated chemical conversion of the related solids and specifies their characteristics.

Wide use of (2) points to its sufficiently high generality and, consequently, makes practical applications of the suggested method more than feasible. Nor is the generality we have mentioned surprising, for (2), in its meaning, corresponds to the Arrhenius equation. The method of finding A and E does not necessarily require larger amounts of experimental data. As the example considered shows, a set of data used in thermal analysis and obtained at different rates of temperature rise is quite sufficient to perform standard computations. By calculating the correlation coefficient for (2), cases can be found when the suggested method does not give a positive result. In particular, this may be due to the fact that the changed experimental conditions alter the nature of the process which controls the heat conversions of the substance under study.

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Zusammenfassung — Es wird eine Methode zur Berechnung der Arrhenius-Parameter vorgeschlagen, die auf der Auswertung der durch Lösung des inversen kinetischen Problems bestimmten Koordinatenabschnitte mit weit ausgedehnten Konfidenzbereich beruhen. Die Anwendbarkeit dieser Methode wird an Hand eines Vergleichs der Arrhenius-Parameter demonstriert, die aus von anderen Autoren mitgeteilten nicht-isothermen und isothermen Daten erhalten wurden.

Резюме — Предложен метод нахождения аррениусовых параметров, основанный на оценке положения места пересечения вытянутых доверительных областей, получающихся при решении обратной кинетической задачи. Эффективность метода проиллюстрирована путем сравнения полученных этим методом аррениусовых параметров из данных неизотермических экспериментов с данными изотермических опытов, опубликованными в литературе.