Thermochimica Acta, 92 (1985) 157-160
Elsevier Science Publishers B.V., Amsterdam

ANALYSIS AND DEVELOPMENT OF EFFECTIVE INVARIANT KINETIC PARAMETERS FINDING METHOD BASED ON THE NON-ISOTHERMAL DATA

Sergei V.Levchik, Galina F.Levchik and Anatolii I.Lesnikovich
Institute of Physico-Chemical Problems, Byelorussian State University,* Minsk, U.S.S.R.

ABSTRACT

The connection of the method of estimating effective invariant kinetic characteristics with the common ways of describing the complicated process by means of multiparametric dependences and the main equation of non-isothermal kinetics is discussed. This method gives the possibility to transform variables, which makes the statement inverse kinetic problem conditions better. The validity of the method has been shown by the experimental data of the butyl rubber decomposition.

INTRODUCTION

It is known that the inverse kinetic problem belongs to the clan of the mathematical problem characterized by a poor statement of its conditions and, therefore, such problem have no unique solution unless special methods are used [1]. The poor statement of the problem conditions determines its solution in the form of a greatly extended confidence 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. There is an apparent compensative effect in this case

$$\log A = B + eE, \quad (1)$$

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 pencils, whose centers lie on one straight line:

$$B = f - ge. \quad (2)$$

That has been shown in [2] by an example of kinetic data applied to heterogeneous catalytic reactions and in [3-5] by an example of thermolysis of crystalline substances data in non-isothermal conditions. It is evident, that this straight line is Arrhenius line also and it specifies the invariant kinetic parameters ($g = E_i$ and $f = \log A_i$) at the changing experimental conditions.

Proceedings of ICTA 85, Bratislava

ANALYSIS AND DEVELOPMENT OF THE METHOD

From the geometric consideration it is obvious, that the pencil of lines corresponds in three-dimensional space to a set of the hyperbolic paraboloid plane sections, which is the response function of two variables. Equation of the hyperbolic paraboloid is two-parametric polylinear function [6]:

$$f = f_0 + a_1x_1 + a_2x_2 + + a_{12}x_1x_2 \qquad (3)$$

where f_0 is the standart values of function, x_1 and x_2 are the variables and a_1, a_2, a_{12} are the constants. Formation of the Arrhenius lines pensil in consequence of poor statement of the inverse kinetic problem provides appearence in linearized equation a term which determines interaction of variables. Actually, the reason of the new term appearence is statistical indistinguishable correlation factors at the discrimination of the kinetic functions $f(\alpha)$. Linearized form of the Arrhenius equation with the account of the above mentioned is

$$\log \frac{d\alpha}{dt} = \log A - \frac{E}{2.3RT} + \log f(\alpha) + a_{12}\frac{E}{2.3RT}\log f(\alpha) \qquad (4)$$

where a_{12} is the term, determining interaction of the variables $1/T$ and $\log f(\alpha)$.

It is known, that the second degree geometric surfaces in a common case has four values that is invariant at the parallel transfer and turning of Cartesian axis [7]. It is easily to show, that hyperbolic paraboloid has only two of these values. We shall observe with the help of the equation (4) the values which retain invariant during the parallel transfer of Cartesian axis so as the linear dependence between the points corresponding to the centers of saddle in the different systems of coordinates will keep. That transfer is identical of the realization of eq.(2). Eq.(4), corresponding to [6] may be rewritten as containing the product of two sum:

$$\log \frac{d\alpha}{dt} = \log A - \Delta\log \frac{d\alpha}{dt} +$$

$$\Delta\log \frac{d\alpha}{dt}\left(1 - \frac{1}{\Delta\log \frac{d\alpha}{dt}}\frac{E}{2.3RT}\right)\left(1 + \frac{1}{\Delta\log \frac{d\alpha}{dt}}\log f(\alpha)\right) \qquad (5)$$

where $a_{12} = \Delta\log (d\alpha/dt)$ corresponds the difference between the choosed standart values $\log (d\alpha/dt)_0 = \log A$ and the value of $\log (d\alpha/dt)$, corresponding the centre of Arrhenius line pencil. $\log (d\alpha/dt)$ becomes independent of second variable if one of the term in bracket equal zero.

It is easily to show, that the parameters of compensation effect B and e correspond to the center of pencil coordinates or to the center of hyperbolic paraboloid saddle. In this case we have:

$$B = \log A - \Delta\log \frac{d\alpha}{dt} \qquad (6)$$

$$e = \frac{\Delta\log \frac{d\alpha}{dt}}{E}. \qquad (7)$$

Eliminating $\Delta\log(d\alpha/dt)$ from eq.(6) and (7) interdependence of B on e is obtained:

$$B = \log A_i - E_i e. \qquad (8)$$

If $\log A_i$ and E_i are constant eq.(8) conforms to eq.(2). These are the values, which remain invariant at transfer of the coordinates center towards all direction to the proportional distance.

In ref.[4] has been shown, that the method of finding invariant kinetic parameters corresponds in the particular case of the description of three-factor experiment by polylinear function. This particular case, as in ref.[1], results in transformation of variables to $T^* = \frac{T - \hat{T}}{\hat{T}}$. However, $\hat{T}$ in contrast to $\bar{T}$, is isoparametric and not mean or harmonic mean value. If eq.(2) or (8) are fulfilled the value T would be dependent on the experimental conditions. In ref. [4] has been shown, that this dependence may be result in the further increase of the determinant of information matrix and in the improvement conditionality of the inverse kinetic problem. The fact of geometrical improvement conditionality of the inverse kinetic problem at crossing some elliptic confidence region (1) has been illustrated in paper [2].

RESULTS AND DISCUSSION

The main problem which takes place at the practical application of the method of evaluation invariant kinetic parameters is reality of existence of the relation (2). In this paper the correlation between B and e is suggested by means of thermodestraction of the polymer substance - butyl rubber. As mentioned above, the reason of arising compensation effect in this case is statistical indistinguishable of the correlation factors at choosing of $f(\alpha)$. Relation (2) fulfils with the help of changing heating rate in non-isothermal experiment.

Study is carried out on derivatograph. The portion of the rubber (~100 mg) is placed in platinum crucible and the inert atmosphere is created by argon. Figure 1 illustrates dependence of B on e for the butyl rubber thermolysis at ten different heating rate (after statistical removing of the unsatisfactory points).

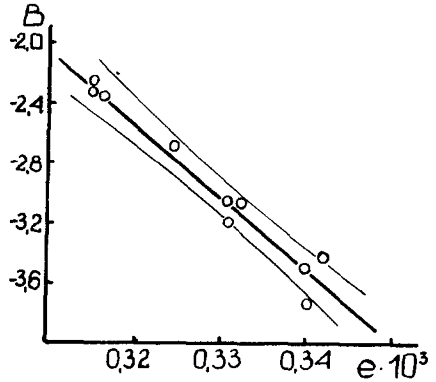

Fig.I. The plot of B on e for the butyl rubber thermodestraction

Calculated as suggested in [4,5] values of the invariant parameters are E_i = 195±25 kJ mol^{-1}, log (A/s^{-1}) = 12±2. The most probable function f(α) is kinetic equation of Avrami-Erofeev (A_3).

In conclusion we note, that according to sence of f = log A_i and g = E_i the main equation of non-isothermal kinetic by means of the substitution eq.(1) and (2) is transformed to:

$$\frac{d\alpha}{dt} = A_i \exp(-\frac{E_i}{RT_k}) \exp(\frac{E_j}{RT_k}) \exp(-\frac{E_j}{RT}) f_j(\alpha) \quad (9)$$

where T_k = 1/2.3Re_k for the substance characterizes the experimental conditions, E_j characterizes the calculation method and the kinetic function. With the proper choice of $f_j(\alpha)$, the terms including T_k are cancelled. Thus, these terms decrease the ambiguity of the inverse kinetic problem solution.

REFERENCES

1 D.M. Himmelblau, Process Analysis by Statistical Methods, John Wiley, New York 1970
2 A.I. Lesnikovich, Zh. Fiz. Khim. 55 (1981) 1165 (in Russian)
3 A.I. Lesnikovich, S.V. Levchik, J. Thermal Anal. 27 (1983) 89
4 A.I. Lesnikovich, S.V. Levchik, V.G. Guslev, Thermochim. Acta 77 (1984) 357
5 A.I. Lesnikovich, S.V. Levchik, V.G. Guslev, V.P. Bobryshev, Dokl. Akad. Nauk BSSR 28 (1984) 647 (in Russian)
6 V.A. Palm, Base of Organic Reactions Quantative Theory, Khimiya, Leningrad, 1977 (in Russian)
7 G.A. Korn, T.M. Korn, Mathematical Handbook for Scientists and Engineers, cM. Craw-Hill Book Company, Inc., New York 1961