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Note

ESTIMATION OF THE PRE-EXPONENTIAL FACTOR IN THE ISOCONVERSIONAL CALCULATION OF EFFECTIVE KINETIC PARAMETERS

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A simple method is suggested for the estimation of the pre-exponential factor, whose value corresponds exactly to the activation energy found by the isoconversional method. The method relies on the application of the apparent compensation relationship. The reliability of the method is verified by model data. It is also found that the kinetic parameters obtained in the isoconversional approach (taking account of the suggested estimation of the pre-exponential factor) agree with the invariant kinetic parameters obtained by earlier methods.

In [refs. 1–6] the so-called isoconversional methods are suggested for the calculation of kinetic parameters from the data of several non-isothermal tests. These methods imply that the basic non-isothermal kinetics equation may be written as

$$\ln\left[\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{ij}\beta_j\right] = \ln[A\,f(\alpha_i)] - (E/RT_{ij}) \tag{1}$$

where β_j is the heating rate in the j-th test, T_{ij} and α_i (temperature and degree of decomposition) are the coordinates of the ith experimental point on the j-th kinetic curve, $f(\alpha)$ is the formal model of the process and A and E are effective kinetic parameters. In the case of a constant process mechanism and equal degrees of decomposition for different heating rates, the activation energy E, whose value is independent of the form of the formal process model $f(\alpha)$, can be estimated from eqn. (1) or by corresponding integral anamorphosis [4–6]. The possibility of such an unambiguous assessment of E using isoconversional methods makes them superior to the approaches based on the explicit formal model of a process (as the choice of the model by experimental data is, in general, ambiguous).

Isoconversional methods, however, do not allow unambiguous estimation of the pre-exponential factor since its calculation is inevitable related to the particular form of the process model (cf. eqn. (1)). The variation in the pre-exponential factor depending on the form of the model may be very

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important. Attempts to overcome this problem through averaging [4,7] can hardly be regarded as reasonable. It is preferable, in this case, to calculate the kinetic parameters by any method (using the explicit form of the formal model), with a subsequent choice of the model that yields an activation energy equal to the value obtained by the isoconversional method. In this case, the values of pre-exponential factor are chosen in conformity with this model. A similar procedure is applied in ref. [8]. Its shortcoming is that the kinetic parameters vary discretely with the changing form of the formal model of the process and it is not always possible to find the model providing the activation energy value which exactly coincides with the value obtained by the isoconversional method.

In view of the above difficulties, a simple method is suggested for the estimation of the pre-exponential factor, independent of the particular form of the process model, which exactly corresponds to the activation energy defined by the isoconversional method. The reliability of the suggested method is verified by model data.

The approach proposed for the estimation of the pre-exponential factor for isoconversional methods is based on the use of the apparent compensation relationship [9] which is the consequence of the application of the Arrhenius equation [10]. In accordance with the compensation relationship

$$\log_{10} A = aE + b \tag{2}$$

only one value of $\log_{10} A$ corresponds to each E value. Therefore, using eqn. (2), a pre-exponential factor can be estimated to correspond exactly with the activation energy found by the isoconversional method. a and b in eqn. (2) are the parameters of the linear regression for which the set of $\log_{10} A$ and E values may be obtained by any method of kinetic parameter calculation based on the variation of the explicit form of the model.

The suggested method was verified by the formal model whose integral form is

$$g(\alpha) = C_1\left[3(1-(1-\alpha))^{1/3}\right] + C_2\left[1.5\left(1-(1-\alpha)^{1/3}\right)^2\right] \tag{3}$$

where $C_1 = C_2 = 0.5$. This process fails to be described by any of the elementary formal models recommended for kinetic analysis [11] since it is a combination of two processes, such as phase boundary reaction and diffusion. Therefore, the kinetic parameters estimated through the methods based on the explicit formal model will not agree with the model values of $E = 125.4$ kJ mol^{-1} (30 kcal mol^{-1}) and $A = 10^{15}$ min^{-1}.

The isoconversional method [6] was used to obtain activation energies from non-isothermal data (five heating rates) modelled in accordance with eqn. (3). The E values so obtained changed slightly (125.2 to 125.3 kJ mol^{-1}) for nine equidistant degrees of decomposition between 0.1 and 0.9.

TABLE 1

The $\log_{10} A$ values obtained at different heating rates calculated by means of apparent compensation relations

β (deg min^{-1})	a (mol kcal^{-1})	b	$\log_{10} A$
1.25	0.5486	−1.5782	14.858
2.50	0.5391	−1.2931	14.858
5.00	0.5296	−1.0092	14.858
10.00	0.5201	−0.7254	14.857
20.00	0.5106	−0.4415	14.856

The values of the pre-exponential factor for 20 formal models cited in ref. 11 were found to be within $10^{13.4}$ to $10^{16.2}$ min^{-1}.

The application of the Coats–Redfern [12] approach, by varying $g(\alpha)$, yielded a and b values in relation (2) (Table 1). It is seen from Table 1 that the values of $\log_{10} A$ obtained in accordance with eqn. (2) as well as the E values cited above agree fairly well with the model values. Therefore, it seems reasonable to suggest that the isoconversional method complemented with the above procedure for the estimation of the pre-exponential factor, could be used for the calculation of the effective values of kinetic parameters.

It should be noted that the kinetic parameters found in the Coats–Redfern approach through statistic discrimination of formal models were $E = 27.6$ kJ mol^{-1}, $\log_{10} A = 2.2$ (the Avrami–Erofe'ev model with the power exponent 1/4) and $E = 38.9$ kJ mol^{-1}, $\log_{10} A = 3.8$ (the Avrami–Erofe'ev model with the power exponent 1/3). The discrimination was made over the residual sum of squares in terms of the Fischer criterion [13]. The difference between the two Avrami–Erofe'ev models is insignificant. Therefore, the calculation procedure based on the explicit form of the formal model process gives an error of not less than 200% for the activation energy and of not less than 300% for the logarithm of the pre-exponential factor.

It is worth noting that the compensation parameter (eqn. (2)) changes with heating rate while the values of the pre-exponential factor remain practically constant. This shows that isoconversional calculation methods yield activation energies $\hat{E}$ corresponding to an isoparametric point [9] (Fig. 1). The application of the isoparametric values of the activation energy $\hat{E}$ and the pre-exponential factor $\hat{A}$ underlies the earlier method of invariant kinetic parameters [14]. These values are defined as the coordinates of the point of intersection of the compensation relations (eqn. (2)) for different heating rates (Fig. 1). The invariant kinetic parameters calculated by the same model data are $\hat{E} = 125.1$ kJ mol^{-1} and $\log_{10} \hat{A} = 14.84$. The coincidence between these values and the kinetic parameters estimated by the isoconversional method (including the method of estimation of the pre-exponential factor) indicates a genetic connection between the method of

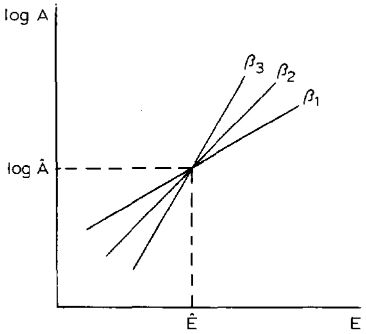

Fig. 1. The $\log_{10} A$ value of the isoparametric point $(\hat{E}, \log_{10} \hat{A})$ does not depend on the heating rate β.

invariant kinetic parameters and the isoconversional methods. This connection was found experimentally [15].

The following conclusions can be drawn. The application of the apparent compensation relationship makes it possible to obtain the values of the pre-exponential factor which correspond exactly with the activation energy estimated by the isoconversional method (both kinetic parameters are in fine agreement with model values), and to connect the isoconversional methods with the method of invariant kinetic parameters.

REFERENCES

1 H.L. Friedman, J. Polym. Sci. Part C, (1963) 183.
2 H.E. Kissinger, Anal. Chem., 29 (1957) 1702.
3 H.C. Anderson, J. Polym. Sci., Part C, (1963) 175.
4 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
5 J.H. Flynn and L.A. Wall, J. Res. Nat. Bur. Stand. Sect. A, 70 (1966) 487.
6 A. Romero, E. Garcia and A. Irabien, Thermochim. Acta, 73 (1984) 101.
7 J.D. Cooney, M. Day and D.M. Wiles, J. Appl. Polym. Sci., 29 (1984) 911.
8 J. Leyko, M. Maciejewski and R. Szuniewicz, J. Therm. Anal, 17 (1979) 263.
9 A.I. Lesnikovich and S.V. Levchik, J. Therm. Anal., 30 (1985) 237, 677.
10 J. Pysiak and B. Sabalski, J. Therm. Anal., 17 (1979) 287.
11 M.E. Brown, D. Dollimore and A.K. Galwey, Reactions in Solid State, Elsevier, Amsterdam, 1980.
12 A.W. Coats and J.P. Redfern, Nature, 201 (1964) 68.
13 N.L. Johnson and F.C. Leone, Statistics and Experimental Design in Engineering and the Physical Science, Vol. 1, Wiley, New York, 1977.
14 A.I. Lesnikovich and S.V. Levchik, J. Therm. Anal., 27 (1983) 89.
15 A.I. Lesnikovich, S.V. Levchik and G.F. Levchik, J. Appl. Polym. Sci., 31 (1986) 1943.