*Journal of Thermal Analysis, Vol. 34 (1988) 609–618*

# COMPLEMENTARITY METHODOLOGY AS APPLIED FOR SOLUTION OF THE INVERSE PROBLEM FOR SOLID-PHASE REACTION KINETICS III

## General analysis of the method of invariant kinetic parameters

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

INSTITUTE FOR PHYSICO-CHEMICAL PROBLEMS OF THE BYELORUSSIAN STATE UNIVERSITY, MINSK, U.S.S.R.

(Received April 22, 1987)

Mathematical analysis has shown that invariant kinetic parameters (IKP) correspond to the real kinetic curve even in the case when the equation prescribing this curve is not used for the calculation of parameters. It has been proved that IKP values coincide with those obtained for isothermal conditions. The theory is verified by calculations using model experimental data. The IKP stability to random experimental errors is studied.

References [1, 2] deal with the method of calculating effective values of kinetic parameters (activation energy and pre-exponential factor) of a solid phase process by data of several non-isothermal tests at various heating rates. It is characteristic of these parameters that the parameters so calculated are invariant with respect both to the actual form of the formal model of the process (i.e. their calculation does not require the knowledge of a particular form of the model) and to the heating rate. In both cases the existence of the invariance resulted in such advantages as unnecessary discrimination of formal models of the process in case of ambiguous solution of the inverse kinetic problem and coincidence of the IKP values with the effective values of Arrhenius parameters for corresponding isothermal conditions. These advantages were found by analysing experimental data for several particular processes [1–3]. In Ref. [4] the relationship between the IKP technique and complementarity methodology providing explanation to the invariance of the obtained parameters is dwelt upon in detail.

*John Wiley & Sons, Limited, Chichester*
*Akadémiai Kiadó, Budapest*

## Mathematical IKP analysis

The temperature dependence of the process rate is traditionally described by the Arrhenius equation [5] having the following form for nonisothermal experimental conditions:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{1}$$

where $\alpha$ is the degree of conversion, $T$ is the temperature, $R$ is the universal gas constant, $\beta$ is the heating rate, $f(\alpha)$ is the formal model of process, $A$ and $E$ are the kinetic parameters. In formal kinetic analysis of solid-phase processes, some set of formal models is usually used which, in accordance with (1), comply with numerous values of $A$ and $E$ related by the apparent compensation effect:

$$\ln A = aE + b \tag{2}$$

where parameters $a$ and $b$ are consistent with isoparametric values of temperature ($\hat{T}$) and rate coostant ($\hat{K}$) [6]

$$\hat{T} = \frac{1}{aR}, \qquad \ln \hat{K} = b$$

Changes of the heating rate cause changes of the parameters in Eq. (2) and, correspondingly, variations of isoparametric temperature and rate constant values. The relationship between them is, in its sense, of the Arrhenius form provided that the process is independent of the heating rate:

$$\ln \hat{K} = \ln \hat{A} - \frac{\hat{E}}{R\hat{T}} \tag{3}$$

where $\hat{A}$ and $\hat{E}$ are the invariant kinetic parameters.

Let us present (1) in a logarithmic form

$$\ln K(T) = \ln A - \frac{E}{RT} \tag{4}$$

where

$$\ln K(T) = \ln\left[\frac{d\alpha}{dT}\cdot\frac{\beta}{f(\alpha)}\right]$$

The existence of the apparent compensation effect (2) suggests the existence of a common intersection point for Arrhenius relations of type (4) for different formal models $f_i(\alpha)$ (Fig. 1). The intersection of these relations is referred to as isoparametric. It is evident that for an isoparametric point the following condition

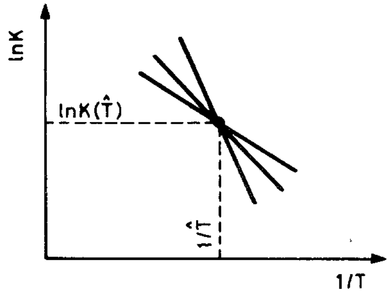

**Fig. 1** Apparent compensation effect as the intersection of Arrhenius relations

holds:

$$\ln K_i(\hat{T}) \approx \text{const} = \ln K(\hat{T}) \tag{5}$$

where $\ln K(\hat{T})$ is the abscissa of the isoparametric point (Fig. 1), $\ln K_i(\hat{T})$ is the abscissa of the rate constant logarithm for different formal models $f_i(\alpha)$ at isoparametric temperature $\hat{T}$.

Let there exist some complex process strictly obeying the kinetic model $f^\circ(\alpha)$ for a certain $\alpha$ range and having effective Arrhenius parameters $E^\circ$ and $A^\circ$. Let us assume further that the mechanism of this process and its parameters are constant both during the transition from isothermal to nonisothermal conditions and within some temperature range (for isothermal conditions) as well as heating rates (for nonisothermal conditions). We shall show that the IKP coincide:

a) with effective parameters $A^\circ$ and $E^\circ$ of a real process even if the process model $f^\circ(\alpha)$ is not a member of models set $f_i(\alpha)$ used for the formal-kinetic analysis;

b) with isothermal values of kinetic parameters.

a) Let $f^\circ(\alpha)$ be disregarded in $f_i(\alpha)$. Assume, that the set $f_i(\alpha)$ is sufficiently representative, i.e. it considers all main types of solid-phase processes. Then, it can reasonably be assumed that $f^\circ(\alpha)$ is not linearly independent of $f_i(\alpha)$, or

$$\int_{\alpha_1}^{\alpha_2} f^\circ(\alpha)\cdot f_i(\alpha)\,\mathrm{d}\alpha \neq 0 \tag{6}$$

Taking into account the connection of the rate constant and formal model of the process, (6) yields:

$$\int_{T_1}^{T_2} K^\circ(T)\cdot K_i(T)\,\mathrm{d}T \neq 0 \tag{7}$$

where $K^\circ(T)$ is the effective rate constant consistent with the real process ($f^\circ(\alpha)$), $T_1$ and $T_2$ the temperatures corresponding to $\alpha_1$ and $\alpha_2$ range of $\alpha$ values where the real process strictly obeys the model $f^\circ(\alpha)$. It follows in a straightforward way from (7) that we have:

$$K^\circ(T) = \sum_i C_i K_i(T) \tag{8}$$

For isoparametric temperature $\hat{T}$ (8) with respect to Eq. (5) may be written as follows:

$$K^\circ(\hat{T}) \approx K(\hat{T}) \sum_i C_i \tag{9}$$

Introducing the normalization condition

$$\sum_i C_i = 1$$

where $C_i$ characterizes partial contribution of the $i$-constant of the rate, gives

$$K^\circ(\hat{T}) \approx K(\hat{T}) \tag{10}$$

So, it follows that the Arrhenius relationship in Eq. (4) for the formal model $f^\circ(\alpha)$, which strictly corresponds to the real process, always passes through the isoparametric point with the precision given by Eq. (5). As Eq. (10) can be extended to any heating rate $\beta$, and the process mechanism $f^\circ(\alpha)$ and its parameters $A^\circ$, $E^\circ$ are stipulated to be constant for some range of $\beta$, then the following statement holds for this range. All the isoparametric points obtained for the range of heating rates and decomposition degrees, for which the process mechanism and kinetic parameters remain constant, lie on the Arrhenius relationship characterized by kinetic parameters $A^\circ$ and $E^\circ$. So, the IKP obtained from the Arrhenius relationship which passes through isoparametric points and, corresponds to different heating rates with the precision given by Eq. (5) coincide with the effective values of kinetic parameters $A^\circ$, $E^\circ$.

b) Assume that the isothermal process proceeds at isoparametric temperatures in accordance with the formal model $f^\circ(\alpha)$ and parameters $E^\circ$, $A^\circ$, i.e. the Arrhenius relationship of the following type holds:

$$\ln K = \ln A^\circ - \frac{E^\circ}{R\hat{T}} \tag{11}$$

On the other hand, with regard for (10), for nonisothermal process equality

$$\ln K(\hat{T}) = \ln \hat{A} - \frac{\hat{E}}{R\hat{T}} \tag{12}$$

can be written, or taking into account the equation proved above in (a)

$$\ln K(\hat{T}) \approx \ln A^\circ - \frac{E^\circ}{R\hat{T}} \tag{13}$$

is valid for the nonisothermal process. Comparison of (13) and (11) yields

$$\ln K(\hat{T}) \approx \ln K \tag{14}$$

So, the Arrhenius relationship to determine IKP values coincides with similar relationships for the isothermal conditions. In other words, the isoparametric value of logarithm of the effective rate constant coincides with the value obtained from an isothermal experiment at isoparametric temperature.

## Modelling nonisothermal kinetic curves

In order to support the above theoretical considerations, five kinetic curves $\alpha$ *vs.* $T$ for five heating rates (1.25, 2.5, 5.0, 10.0 and 20.0 deg·min$^{-1}$) were modelled in accordance with the equation

$$\alpha = G\left[\frac{A}{\beta}\int\limits_0^T \exp\left(-\frac{E}{RT}\right)\mathrm{d}T\right] \tag{15}$$

where function $G$ is the inverse of the integral form of the kinetic function $g(\alpha)$, i.e. $G(g(\alpha)) = \alpha$.

The integral in (15) is replaced by the approximation suggested in [7]

$$\int\limits_0^T \exp\left(-\frac{E}{RT}\right)\mathrm{d}T \approx \frac{E}{R}\frac{\exp(-x)}{x}\,\frac{x^3+18x^2+88x+96}{x^4+20x^3+120x^2+240x+120}$$

where $x = \dfrac{E}{RT}$.

It was assumed that the model of the process obeys the following kinetic equation:

$$g(\alpha) = c_1[3(1-(1-\alpha)^{1/3})]+c_2[1.5(1-(1-\alpha)^{1/3})^2] \tag{16}$$

which is a linear combination of the contracting sphere and Jander equations [8]. The choice of a linear combination is due to the fact that [16] defined complex kinetics and the kinetic curves simulated in conformity with it will be consistent with none of the elementary formal models used for kinetic analysis (cf. [8, 9]). It seems that in this case, discrimination of formal process models to choose the "best" one becomes meaningless at all, hence, hinders the determination of kinetic parameters consistent with the real kinetic curve.

### *Comparison of the traditional and nontraditional methodologies for solution of the inverse kinetic problem*

Using the kinetic curves modelled in accordance with (15) and (16) and plotting $E = 30$ kcal·mol$^{-1}$, $A = 10^{15}$ min$^{-1}$ and three different combinations of coefficients $C_1$ and $C_2$ in (16) (0.3, 0.7; 0.5, 0.5; 0.7, 0.3), we compared the results of calculations using traditional and nontraditional [4] methodologies for solution of the inverse kinetic problem. We used the IKP method with the above algorithm as a nontraditional approach. The traditional methodology will be represented by the widely used Coats–Redfern method [10] with subsequent discrimination of formal models in the values of the residual sums of squares.

In IKP calculations in conformity with the above algorithm, Eq. (1) was replaced by the Coats–Redfern integral anamorphosis [10]. The IKP values obtained for three combinations of coefficients $C_1$ and $C_2$ were $E = 29.91$, $\log A = 14.96$ (0.3, 0.7); $E = 29.93$, $\log A = 14.84$ (0.5, 0.5); $E = 29.90$, $\log A = 14.72$ (0.7, 0.3). Good agreement of invariant and model values of kinetic parameters support the above statement on the coincidence of invariant kinetic parameters with effective ones described by the real kinetic curve.

The calculations by the Coats–Redfern method were performed as follows. For each formal model (Table 1) presented in Eq. (17)

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\frac{AR}{\beta E} - \frac{E}{RT} \tag{17}$$

the values of $A$ and $E$ were fitted by the least squares method. As an example, Table 1 gives the values of $E$, $\log A$ and residual sum of squares $S^2$ for the combination of coefficients $C_1 = 0.5$, $C_2 = 0.5$ and heating rate $\beta = 2.5$ deg·min$^{-1}$. The Fischer criterion was used for discrimination [11]. Formal models which do not satisfy the condition

$$\frac{S_i^2}{S_{\min}^2} \leqslant F \tag{18}$$

**Table 1** Results of kinetic parameters calculation by means of Coats–Redfern method

| $N$ | Formal model | $E$, kcal/mol | Log $A$ | $S^2$ |
|---|---|---|---|---|
| 1 | $\alpha^{1/4}$ | 4.31 | 0.74 | 0.00403 |
| 2 | $\alpha^{1/3}$ | 6.28 | 1.93 | 0.00708 |
| 3 | $\alpha^{1/2}$ | 10.23 | 4.20 | 0.01572 |
| 4 | $\alpha$ | 22.06 | 10.71 | 0.06211 |
| 5 | $\alpha^{3/2}$ | 33.89 | 17.08 | 0.13918 |
| 6 | $[-\ln(1-\alpha)]^{1/4}$ | 6.56 | 2.17 | 0.00025 |
| 7 | $[-\ln(1-\alpha)]^{1/3}$ | 9.28 | 3.77 | 0.00047 |
| 8 | $[-\ln(1-\alpha)]^{1/2}$ | 14.72 | 6.86 | 0.00110 |
| 9 | $[-\ln(1-\alpha)]^{1/1.5}$ | 20.16 | 9.89 | 0.00200 |
| 10 | $1-(1-\alpha)^{1/2}$ | 26.11 | 12.75 | 0.01455 |
| 11 | $1-(1-\alpha)^{1/3}$ | 27.65 | 13.45 | 0.00428 |
| 12 | $-\ln(1-\alpha)$ | 31.04 | 15.86 | 0.00460 |
| 13 | $(1-\alpha)^{-1/2}-1$ | 36.87 | 18.88 | 0.10136 |
| 14 | $(1-\alpha)^{-1}-1$ | 43.58 | 22.97 | 0.39570 |
| 15 | $((1+\alpha)^{1/3}-1)^2$ | 41.30 | 19.89 | 0.29037 |
| 16 | $\alpha^2$ | 45.72 | 23.38 | 0.24691 |
| 17 | $(1-\alpha)\ln(1-\alpha)$ | 50.65 | 25.88 | 0.12640 |
| 18 | $1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}$ | 52.71 | 26.39 | 0.07976 |
| 19 | $(1-(1-\alpha)^{1/3})^2$ | 56.92 | 28.76 | 0.01670 |

were discriminated ($S_i^2$ is the residual sum of squares corresponding to the $i$-th kinetic function; $S_{\min}^2$ the minimum residual sum of squares among all $S_i^2$; $i$ is the serial number of the formal model; $F$ the tabulated Fischer criterion).

Thus, for the case $C_1 = 0.5$, $C_2 = 0.5$ with respect to condition (18), the Avrami–Erofeev model ($A_m$) with $m = 4$ and 3 (NN 7, 8 in Table 1) are the "best" one for all the heating rates. For these models, irrespective of the heating rate, $E$ and $A$ are equal to 6.6 kcal · mol$^{-1}$, $10^{2.2}$ min$^{-1}$ ($A_4$) and 9.3 kcal · mol$^{-1}$, $10^{3.8}$ min$^{-1}$ ($A_3$), respectively. The advantage of the IKP method which represents for this instant the nontraditional methodology applying the complementarity principle to solve the inverse kinetic problem is evident.

It is also worth to note that the suggestion made in part I [12] to use the Avrami–Erofeev model as a generalized description has restrictions as seen from the above example. This means that the Avrami–Erofeev model cannot always be used as an approximation [12] to the nontraditional methodology of solving the inverse kinetic problem.

### *Relationship between kinetic parameters and parameters obtained in isothermal experiment*

It has been proved above that the isoparametric value of the rate constant coincided with its isothermal value at the isoparametric temperature (see Eq. (14)). To verify this statement, isoparametric values of $\hat{T}$ and $\ln \hat{K}(T)$ were calculated by (2) and compared with the logarithm of the rate constant of the isothermal process characterized by the values of kinetic parameters consistent with model ones $E = 30$ kcal · mol$^{-1}$, $A = 10^{15}$ min$^{-1}$. So, the dependence of the logarithm of the rate constant of the isothermal process on isoparametric temperature is

$$K = 15 - \frac{30000}{R\hat{T}} \tag{19}$$

The results of the calculation for $C_1 = 0.5$, $C_2 = 0.5$ are cited in Table 2. The systematic nature of the $\ln \hat{K}(T)$ deviations from $\ln K$ may, presumably, be explained by the systematic error introduced by the approximate Coats–Redfern equation replacing Eq. (1) in IKP calculations. Such errors, however, cause only insignificant deviations of preexponent factor in IKP estimation.

### *Influence of random errors on kinetic parameters obtained by the IKP method*

Below some results are presented which verify the stability of kinetic parameters obtained by the IKP procedure against disturbances introduced by random errors in temperature $T$ and decomposition degree $\alpha$. Random error distribution in $T$ and

**Table 2** Comparative values of isoparametric and isothermal rate constants

| Heating rate, deg/min | Isoparametric values, | | Ln $K$, Eq. (19) | Ln $K$ − Ln $\hat{K}(T)$ |
|---|---|---|---|---|
| | $\hat{T}$, K | Ln $\hat{K}(T)$ | | |
| 1.25 | 398.3 | −3.64 | −3.36 | 0.28 |
| 2.50 | 405.4 | −2.98 | −2.71 | 0.27 |
| 5.00 | 412.6 | −2.32 | −2.05 | 0.27 |
| 10.00 | 420.2 | −1.67 | −1.40 | 0.27 |
| 20.00 | 428.0 | −1.02 | −0.74 | 0.28 |

$\alpha$ was assumed to be normal. Temperature values with an experimental error were estimated according to

$$T_j = T_j^0 + \sigma_T X_j \tag{20}$$

where $T^0$ is the model temperature value, $\sigma_T$ is the rms deviation, $X_i$ is the random number varying in Gaussian distribution.

Similarly, the values of the decomposition degree with an experimental error, were found as

$$\alpha_j = \alpha_j + \sigma_\alpha X_j \tag{21}$$

In this case $\alpha_j^0$ is the model value of the degree of decomposition. The rms temperature deviation $\sigma_T$ and rms decomposition degree deviation $\sigma_\alpha$ were chosen to conform with the recorder error of the derivatograph. For the 500 mg sample in the temperature range from 300 to 600 K the temperature error did not exceed IK, in the degree of decomposition is no more than 0.001. Taking account the fact that the values of normally distributed random numbers have a dispersion $\sigma = 1$, the rms deviations in temperature and degree of decomposition were chosen to be $\sigma_T$ = IK, $\sigma_\alpha = 0.001$.

The values of normally distributed random numbers $X_j$ were obtained using the generator random numbers $R_i$ uniformly distributed within the interval (0.1) [13]

$$X_j = \frac{\sum_{i=1}^{n} R_i - \frac{n}{2}}{\sqrt{\frac{n}{2}}} \tag{22}$$

As noted in Ref. [13], at $n = 12$ Eq. (22) provides satisfactory values of the Gaussian distribution. We have applied the greatest value $n = 48$, because following the central limit theorem [11], distribution (22) asymptotically approaches the normal one with increasing $n$.

Using the IKP method, the values of kinetic parameters were obtained by the model with scattering data for three different combinations of coefficients $C_1$ and $C_2$ in linear combination (16):

$$\log A = 15.08;\ E = 30.41\ \text{kcal}\cdot\text{mol}^{-1}\quad (C_1 = 0.7,\ C_2 = 0.3)$$

$$\log A = 14.50;\ E = 29.31\ \text{kcal}\cdot\text{mol}^{-1}\quad (C_1 = 0.5,\ C_2 = 0.5)$$

$$\log A = 15.76;\ E = 31.68\ \text{kcal}\cdot\text{mol}^{-1}\quad (C_1 = 0.3,\ C_2 = 0.7)$$

So, the disturbances due to simulated errors exert but a slight effect on the values of invariant parameters. However, on interpreting real kinetic curves the errors in kinetic parameters often turn out to be greater which, probably, is resulted in by some changes in the behaviour of the process with changing heating rate.

## Conclusions

Mathematical analysis and modelling of the IKP method show:

(i) the IKP method gives access to the effective values of kinetic parameters of a real solid phase process without using its formal model in an explicit form;

(ii) the IKP isoparametric values of the logarithm of the rate constant used in the IKP method coincide within a small systematic error with the corresponding values of the isothermal process at the isoparametric temperature. Systematic errors seem to be resulted in by the approximate nature of the Coats–Redfern equation used in the IKP calculations;

(iii) the IKP method shows high stability towards experimental errors in $T$ and $\alpha$ values.

These results make the IKP method suitable for the solution of problems requiring reliable estimation of effective kinetic parameters values by data on non-isothermal experiments.

## References

1 A. I. Lesnikovich and S. V. Levchik, J. Thermal Anal., 27 (1983) 89.

2 A. I. Lesnikovich, S. V. Levchik, V. G. Guslev and V. P. Bobryshev, Dokl. AN BSSR, 28 (1984) 647.

3 A. I. Lesnikovich, S. V. Levchik and G. F. Levchik, J. Appl. Polym. Sci., 29 (1984) 911.

4 S. V. Vyazovkin and A. I. Lesnikovich, J. Thermal Anal., 32 (1987) 901.

5 S. Arrhenius, Z. Phys. Chem., 4 (1889) 226.
6 A. I. Lesnikovich and S. V. Levchik, J. Thermal Anal., 30 (1985) 237.
7 G. I. Senum and R. T. Yang, J. Thermal Anal., 11 (1977) 445.
8 B. Delmon, Introduction à la Cinétique Heterogène, Technique, Paris 1969.
9 M. E. Brown, D. Dollimore and A. K. Galwey, Reactions in the Solid State, Elsevier, Amsterdam 1980.
10 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
11 N. L. Johnson and F. C. Leone, Statistics and Experimental Design in Engineering and the Physical Sciences, Wiley, N.Y. 1977.
12 A. I. Lesnikovich, S. V. Vyazovkin and I. S. Romanovsky, J. Thermal Anal., 34 (1988) 85.
13 V. M. Ivanova, Random Numbers and it's Application, Finansy i Statistika, Moskva 1984 (in Russian).

**Zusammenfassung** — Im Ergebnis einer mathematischen Untersuchung wurde festgestellt, daß nonvariante kinetische Parameter (IKP) der realen kinetischen Kurve sogar für den Fall entsprechen, daß die Funktion dieser Kurve nicht zur Parameterschätzung verwendet wurde. Es wurde gezeigt, daß die IKP-Werte mit denen unter isothermen Bedingungen erhaltenen übereinstimmen. Die theoretischen Betrachtungen wurden durch Berechnungen mit experimentellen Modelldaten überprüft. Außerdem wurde die Abhängigkeit der IKP gegenüber experimentellen Randomfehlern untersucht.

**Резюме** — Путем математического анализа показано, что инвариантные кинетические параметры (ИКП) соответствуют реальной кинетической кривой даже в том случае, когда для расчета параметров не использовано уравнение, задающее данную кривую. Доказано, что значения ИКП совпадают со значениями, полученными в изотермических условиях. Теоретические положения подтверждены расчетами на модельных экспериментальных данных. Исследована устойчивость ИКП к случайным ошибкам.