Thermochimica Acta, 211 (1992) 181–187
Elsevier Science Publishers B.V., Amsterdam

Alternative description of process kinetics

S. Vyazovkin

Institute for Physico-Chemical Problems, Byelorussian University, Minsk 220080 (Belarus)

(Received 3 April 1992)

Abstract

The paper provides comparison between the traditional and alternative descriptions of process kinetics. Since the traditional kinetic triplet $E, A, f(w)$ is ambiguous and suitable for simple processes only, it can describe no real kinetics. It is shown that, on the basis of isoconversional methods, the complete kinetic description can be built in the coordinates E, w, T. Because such a description is unambiguous and suitable for both simple and complex processes, it is accepted as an alternative to the traditional approach. Algorithms to transform the alternative description into the traditional form are suggested.

> We are only undeceived
> Of that which, deceiving, could no longer harm.
> T.S. Eliot, *East Coker*

INTRODUCTION

Our investigations [1, 2] have shown that the isoconversional methods (IM) of calculating the Arrhenius parameters occupy a special place in non-isothermal kinetics. As they are capable of elucidating the complex nature [3] of a process and solving applied kinetic problems [4], IM are a unique instrument for kinetic processing of experimental data for real processes [5–8]. However, IM are worthy of close attention not only from the viewpoint of practice, but also from the viewpoint of non-isothermal kinetic theory. On the basis of IM, in terms of the common equation

$$\mathrm{d}w/\mathrm{d}T = A\exp(-E/RT)f(w)/q \tag{1}$$

it is possible to build an alternative kinetic description to the traditional one.

In this paper we consider an alternative description and compare it with the traditional one. To begin with, we will dwell briefly upon the traditional kinetic description of processes.

Correspondence to: S. Vyazovkin, Institute for Physico-Chemical Problems, Byelorussian University, Minsk 220080, Belarus.

TRADITIONAL DESCRIPTION

Equation (1) and its various integral analogues [9, 10] contain three unknown components E, A and $f(w)$, which are estimated by the dependence of dw/dT (or w) on T obtained from thermal analysis (TA) curves. This triplet represents the traditional kinetic description which has become so familiar that the absence of even one of its components causes a feeling of incompleteness of the investigation made. At the same time, we can say with assurance that the theoretical value of the triplet estimated by means of TA data is very poor. In any event, the gross nature of the traditional description's components permits interpretation of neither E, as the energy barrier height, nor A, as the activated complex vibrational frequency nor $f(w)$, as the mechanism of the process [11].

Nevertheless, besides the theoretical problems there is a wide range of practical ones connected with the reconstruction of TA curves at given heating rates or temperatures. The solution of such problems requires the knowledge of all three components of the traditional kinetic description. Let us see to what extent the traditional description is suitable for solving practical problems.

First of all, attention should be drawn to the fact that, from the geometrical viewpoint, the traditional kinetic description is a point in the space $(E, A, f(w))$, which only at first sight seems three-dimensional. Taking into account the apparent compensation dependence [12] with which the calculated values of A and E are always correlated, it should be recognized that in reality the traditional description is a point on the plane E (or A)–$f(w)$. Clearly, this limitation makes us doubt the necessity of using all three components of the traditional kinetic description.

Besides, there are two facts which in general make us doubt the possibility of practical application of the traditional kinetic description. The first fact is associated with the fundamental ambiguity [1, 13, 14] of estimating the above triplet by experimental data. It is shown [15, 16] that the ambiguity of choosing the model of a process $f(w)$ leads to an ambiguity of estimating E and A such that the reconstruction of thermoanalytical curves is impossible.

The second fact makes us doubt the reliability of the traditional description even in the exceptional case where the kinetic triplet has been determined unambiguously. The point is that the kinetic triplet can be a reliable description of a gross-single-stage (simple) process alone. More than that, the traditional kinetic description gives no information about the complex character of the process [5, 17]. For this reason, as well as by virtue of the fact that the majority of real processes are complex, the reliability of TA curve reconstruction in terms of the traditional description is always doubtful [17].

Thus, the traditional kinetic description is unsuitable for reconstructing

TA curves, which, in our opinion, is equivalent to its unsuitability at all. Therefore the need for an alternative kinetic description is indubitable.

ALTERNATIVE DESCRIPTION

The mere use of IM gives only the activation energy. In doing this, one should keep in mind two facts which distinguish this quantity from the activation energy as a component of the traditional kinetic description. Firstly, this quantity is estimated unambiguously; i.e. to calculate it by IM, there is no need to choose the model of a process. Secondly, IM gives not one value of activation energy but a whole set, in which each value of E corresponds to a definite transformation degree w.

Thus, IM permits the dependence $E = E(w)$ to be obtained without choosing the process model. What information about the process does this dependence give?

First of all, this dependence makes it possible to reveal [3] whether the process being investigated is a simple ($E \neq E(w)$) or a complex ($E = E(w)$) one. Additionally, the shape of the dependence of E on w is a source of information on the mechanism of complex processes [3, 5–8, 18]. Thus, the E on w dependence gives information which is wholly unavailable to the traditional kinetic description.

Let us now dwell upon the practical problems connected with reconstructing TA curves at given heating rates or temperatures. To solve them it is not enough to know only the E dependence on w which, naturally, cannot pretend to be a complete description of the process kinetics. One should not forget, however, that we have experimental dependences of $\mathrm{d}w/\mathrm{d}T$ (or w) on T which carry that invaluable kinetic information which was completely rejected by the traditional description, considering that all the information on the process is already contained in the kinetic triplet. Using this information, we can build on the basis of IM an alternative kinetic description which, from the geometrical viewpoint, represents a curve in three-dimensional space (E, w, T).

Reconstructing TA curves within the scope of this description is realized by the algorithms suggested in [4]. Using the dependence of E on w, these algorithms permit transformation of the experimental dependences of w on T into the dependences: w on T at a given heating rate; T on q at a given transformation degree; w on q at a given temperature; w on t at a given temperature; t on T at a given transformation degree; w on T at a given time. The advantage of these algorithms is the fact that they take into account the complex character of a process in reconstructing the above dependences. As a result, the reliability of reconstructing TA curves within the scope of the alternative kinetic description turns out to be much higher [17] compared with that obtained within the scope of the traditional description.

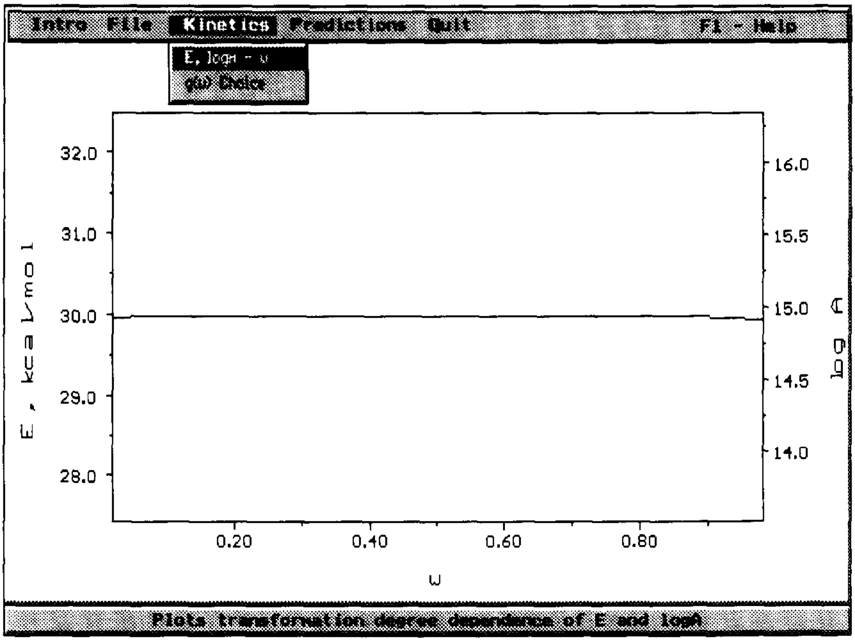
Thus, the alternative kinetic description permits us to obtain information on the mechanism of both simple and complex (real, in other words) processes, as well as to reconstruct TA curves corresponding to them. The only apparent disadvantage of the alternative description is its unaccustomed form, containing neither A nor $f(w)$. Below we suggest simple methods of transforming the alternative description into the traditional form.

TRANSFORMATION OF THE ALTERNATIVE DESCRIPTION INTO THE TRADITIONAL FORM

The traditional kinetic triplet requires estimation not only of E, but also of A and the process model. To estimate the pre-exponent, we will employ the previously proposed method [19] relying on the apparent compensation dependence

$$\ln A = aE + b$$

This relation permits estimation by the known value of the activation energy of the pre-exponent value, which for a simple process will be constant over the entire range of transformation degree, whereas for a complex one it will represent a dependence analogous to that of E on w. The results of the pre-exponent calculation for two model processes are shown in the figures. Figure 1 shows the dependence of E and $\log A$ on w



Plots transformation degree dependence of E and logA

Fig. 1. Dependence of activation energy and pre-exponent on transformation degree for the simple process.

for the first-order simple process with $E = 30\,\mathrm{kcal\,mol^{-1}}$ and $A = 10^{15}\,\mathrm{min^{-1}}$. Figure 2 shows a similar dependence for the complex process incorporating two independent first-order reactions with $E_1 = 30\,\mathrm{kcal\,mol^{-1}}$, $A_1 = 10^{14}\,\mathrm{min^{-1}}$ and $E_2 = 40\,\mathrm{kcal\,mol^{-1}}$, $A_2 = 10^{18}\,\mathrm{min^{-1}}$.

Knowing the values of E and A corresponding to a particular transformation degree w, it is easy to calculate the values of the model function describing the process in both the differential

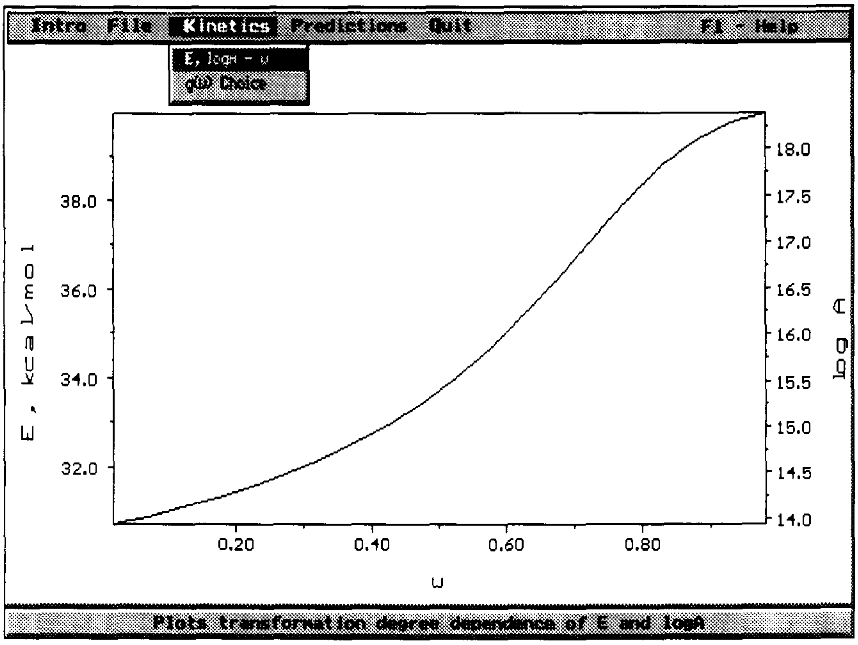
$$f(w) = q\,\mathrm{d}w/\mathrm{d}T/[A\exp(-E/RT)]$$

and the integral forms

$$g(w) = (A/q)\int \exp(-E/RT)\,\mathrm{d}T \qquad (2)$$

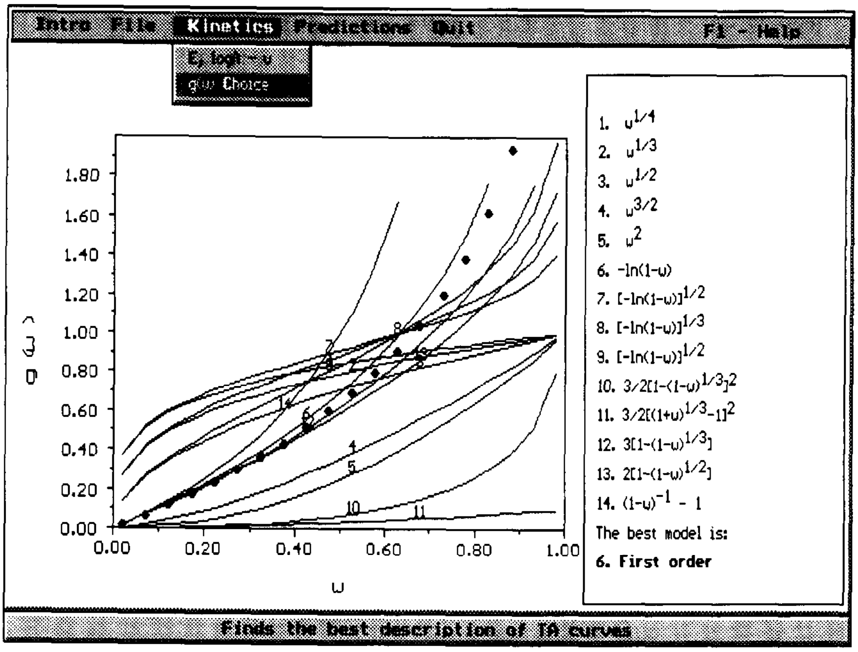
As a result, we obtain the experimental dependence of $g(w)$ (or $f(w)$) on w. The explicit form of the model function is found by selection of the corresponding theoretical equations [9, 10]. In particular, from Fig. 3 it is seen that for the above simple process the dependence of $g(w)$ on w calculated by eqn. (2) is described well by the first-order model.

It should be borne in mind that the methods of transforming the alternative description into the traditional form differ from the methods of estimating the components of the traditional kinetic description. Therefore, correspondence of the transformation results to the kinetic triplet should not be expected.



Plots transformation degree dependence of E and logA

Fig. 2. Dependence of activation energy and pre-exponent on transformation degree for the complex process.



1. $w^{1/4}$
2. $w^{1/3}$
3. $w^{1/2}$
4. $w^{3/2}$
5. w^{2}
6. $-\ln(1-w)$
7. $[-\ln(1-w)]^{1/2}$
8. $[-\ln(1-w)]^{1/3}$
9. $[-\ln(1-w)]^{1/2}$
10. $3/2[1-(1-w)^{1/3}]^2$
11. $3/2[(1+w)^{1/3}-1]^2$
12. $3[1-(1-w)^{1/3}]$
13. $2[1-(1-w)^{1/2}]$
14. $(1-w)^{-1} - 1$

The best model is:

6. First order

Fig. 3. Choice of the best model for the simple process data (points).

CONCLUSIONS

In conclusion, we would like to emphasize that the traditional kinetic description should in no way be regarded as part and parcel of non-isothermal kinetics. Non-isothermal kinetics has inherited it from isothermal kinetics and adapted it to the new conditions by means of the trivial mathematical transformation

$$\mathrm{d}w/\mathrm{d}T = \mathrm{d}w/\mathrm{d}(T_0 + qt) = (\mathrm{d}w/\mathrm{d}t)/q$$

assuming linear temperature variation with time $T = T_0 + qt$. Taking into account this transformation, eqn. (1) can be written in the isothermal form

$$\mathrm{d}w/\mathrm{d}t = A\exp(-E/RT)f(w) \tag{3}$$

but in this case its variables acquire a new meaning different from that which they had in isothermal kinetics. The temperature in eqn. (3) becomes a function of time and the transformation degree and the rate of the process become functions of two variables—time and temperature. This means that the information structure of non-isothermal data differs radically from the structure of isothermal kinetic data. However, correct estimation of the components of the traditional kinetic description requires the isothermal structure of data [11] and, therefore, turns out to be unsuitable in non-isothermal kinetics. This is convincingly evidenced by everyday practice which abounds in examples of unsuccessful kinetic calculations performed on the basis of non-isothermal data within the scope of the traditional kinetic description. But the same practice shows that we would rather deny to non-isothermal kinetics the ability of producing reliable and accurate kinetic information [9] than burst the fetters of the traditional kinetic description. It seems that the time has come to stop deceiving ourselves and to recognize the evident truth that non-isothermal data have a different nature and, consequently, require a kinetic description other than the traditional one.

Perhaps an alternative description may be of another form differing from that suggested in our work, but the suggested variant has already been proved and has demonstrated its workability. It remains only to add that all the above mentioned potentialities of the alternative description, including its transformation into the traditional form, have been realized in the KINTOOL software developed by Vyazovkin and Goryachko [20].

REFERENCES

1 S.V. Vyazovkin and A.I. Lesnikovich, J. Therm. Anal., 35 (1989) 2169.
2 S.V. Vyazovkin and A.I. Lesnikovich, J. Therm. Anal., 36 (1990) 599.
3 S.V. Vyazovkin and A.I. Lesnikovich, Thermochim. Acta, 165 (1990) 273.
4 S.V. Vyazovkin and A.I. Lesnikovich, Thermochim. Acta, 203 (1992) 177.
5 S.V. Vyazovkin and A.I. Lesnikovich and V.A. Lyutsko, Thermochim. Acta, 165 (1990) 17.
6 S.V. Levchik, E.E. Bolvanovich, A.I. Lesnikovich, O.A. Ivashkevich, P.N. Gaponik and S.V. Vyazovkin, Thermochim. Acta, 168 (1990) 211.
7 S.V. Vyazovkin, V.V. Bogdanova, I.A. Klimovtsova and A.I. Lesnikovich, J. Appl. Polym. Sci., 42 (1991) 2095.
8 S.V. Vyazovkin, V.V. Bogdanova, I.A. Klimovtsova and A.I. Lesnikovich, J. Appl. Polym. Sci., 44 (1992) 2157.
9 M.E. Brown, D. Dollimore and A.K. Galwey, in C.H. Bamford and C.F.H. Tipper (Eds.), Comprehensive Chemical Kinetics, Vol. 22, Elsevier, Amsterdam, 1980.
10 J. Sestak, Thermophysical Properties of Solids, Academia Prague, Prague, 1984.
11 S. Vyazovkin, Thermochim. Acta, 200 (1992) 461.
12 A.I. Lesnikovich and S.V. Levchik, J. Therm. Anal., 30 (1985) 677.
13 S.V. Vyazovkin and A.I. Lesnikovich, J. Therm. Anal., 32 (1987) 909.
14 S.V. Vyazovkin, A.I. Lesnikovich and E.A. Gunin, Thermochim. Acta, 130 (1988) 269.
15 S.V. Vyazovkin and A.I. Lesnikovich, Thermochim. Acta, 165 (1990) 11.
16 S.V. Vyazovkin and A.I. Lesnikovich, Thermochim. Acta, 182 (1991) 133.
17 S. Vyazovkin and V. Goryachko, Thermochim. Acta, 194 (1992) 221.
18 S.V. Vyazovkin, V.I. Goryachko and A.I. Lesnikovich, Thermochim. Acta, 197 (1992) 41.
19 S.V. Vyazovkin and A.I. Lesnikovich, Thermochim. Acta, 128 (1988) 297.
20 S. Vyazovkin and V. Goryachko, Int. Labmate, 17 (1992) 21.