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ON THE USE OF DIEFALLAH’S COMPOSITE INTEGRAL METHOD FOR THE NON-ISOTHERMAL KINETIC ANALYSIS OF HETEROGENEOUS SOLID-GAS REACTIONS

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The paper contains an analysis of the used of Diefallah’s composite integral method of kinetic parameters evaluation. It is shown that the application of this method should be preceded by the application of an isoconversional method through which the dependence of the activation energy, E, on the conversion degree, α, should be established. If E depends on α, Diefallah’s composite integral method leads to erroneous results. If E does not depend on α, the true kinetic model should be comprised in the pre-established set of kinetic models. These observations were checked for two sets of non-isothermal data, namely: (a) the TG curves corresponding to the dehydration of $CaC_2O_4 \cdot H_2O$; (b) the TG curves corresponding to the thermal decomposition of polyvinyl chloride (PVC).

Keywords: *heterogeneous solid-gas reactions, non-isothermal kinetics*

Introduction

The kinetic analysis of the non-isothermal experimental data corresponding to a heterogeneous solid-gas reaction occurring in a single step is based on the rate equation [1]:

$$\beta \frac{\mathrm{d}\alpha}{\mathrm{d}T} = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \tag{1}$$

or its integral form:

$$g(\alpha) = \frac{A}{\beta}\int_0^T \left[\exp\left(-\frac{E}{RT}\right)\right]\mathrm{d}T \tag{2}$$

where: α is conversion degree, β – constant heating rate, T – temperature, A – pre-exponential factor, E – activation energy, $f(\alpha)$ – differential conversion function, $g(\alpha) = \int_0^\alpha \frac{\mathrm{d}(\alpha)}{f(\alpha)}$ – integral conversion function, and R – gas constant.

Using as starting point Eqs (1) and (2), various methods of kinetic triplet ($E, A, f(\alpha)$ or $g(\alpha)$) evaluation were developed [1]. Some relatively recent papers [2–6] evidenced the importance of the isoconversional methods (model-free methods), which allow to obtain the dependence of the activation energy on the degree of conversion without the knowledge of the analytical form of $f(\alpha)$ (kinetic model). In order to find $f(\alpha)$ or $g(\alpha)$ there were suggested: (1) procedures for discrimination from a pre-established set of functions of conversion after E was evaluated by means of an isoconversional method [7–13]; (2) Diefallah’s composite integral method, which allow to determine the complete kinetic triplet [14]; (3) the invariant kinetic parameters method (IKP method) [15, 16].

In this paper we are going to analyze the applicability of Diefallah’s composite integral method. The results of such an analysis will be verified for two non-isothermal data, namely: (a) to the dehydration of $CaC_2O_4 \cdot H_2O$; and (b) the dehydrochlorination of PVC.

Some observations concerning the use of Diefallah’s composite integral method

In order to apply this method, it is necessary to record the curves α *vs.* T at several linear heating rates.

The relationship that grounds the method [14] results through the approximation of the temperature integral $\int_0^T \left[\exp\left(-\frac{E}{RT}\right)\right]\mathrm{d}T$ from Eq. (2) either by the expression suggested by Coats and Redfern [17] (composite method I) or by the expression suggested by Doyle [18] (composite method II). For most heterogeneous reactions both approximations led to close results. This is the reason for in the following we will use only composite method I that is based on the relation:

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$$\ln\left[\beta\frac{g(\alpha)}{T^2}\right]=\ln\frac{AR}{E}-\frac{E}{RT} \qquad (3)$$

For each form of the integral function of conversion, $g(\alpha)$, from a pre-established set of kinetic models, the straight line $\ln\left[\beta\frac{g(\alpha)}{T^2}\right]$ *vs.* $(1/T)$ is recorded. In this line the experimental data obtained at all heating rates are included. The right expression of $g(\alpha)$ corresponds to the highest correlation coefficient and to the lowest standard deviation. From the parameters of the straight line the activation parameters, E and A, are obtained.

The following two questionable hypotheses ground Diefallah's composite integral method:

a – the investigated heterogeneous reaction occurs in a single step;

b – the kinetic model characteristic of the investigated change is included in the considered set of functions of conversion.

In order to verify the first hypothesis we should establish the dependence E *vs.* α, using an isoconversional method. If E does not depend on α the hypothesis (a) is fulfilled, and if E depends on α , the mechanism of the investigated change is a complex one (successive or parallel reactions, reversible reactions, etc.). Obviously in this situation Diefallah's composite integral method cannot be applied. Thus, the use of the composite integral method does not exclude the previous use of an isoconversional method. In two very recent papers [19, 20] this order is reversed. It is specified [19] that the deviations from the straight line $\ln\left[\beta\frac{g(\alpha)}{T^2}\right]$ *vs.* $(1/T)$ could be interpreted in term of multi-step reaction mechanism. In this paper we will show that in a case of strong dependence of E on α (dehydration of $CaC_2O_4{\cdot}H_2O$), considering hypothesis (a) as true, Diefallah's method leads to a kinetic triplet (*E, A,* $g(\alpha)$), which does not describe correctly the analyzed heterogeneous change.

The hypothesis (b) is common to all the procedures for discrimination of $f(\alpha)$ from a pre-established set of functions of conversion. This hypothesis could be checked also by using an isoconversional method. It is necessary that the relative deviation (*e*%) of E obtained by Diefallah's method with respect E obtained through the isoconversional method should not exceed 10% (absolute value). If this condition is not fulfilled, it means that the kinetic model characteristic of the investigated change was not in the pre-established set. This last case is met in a very recent work [19] dedicated to the kinetic analysis of the thermal decomposition of CuC_2O_4–ZnC_2O_4 mixture in air (*e*%=19 for CuC_2O_4, *e*%=15% for ZnC_2O_4). In this work the high values of *e*% are assigned erroneously to the model-free method whose use supposes the lack in information concerning the reaction mechanism. However, the importance of the isoconversional methods consists just in their capacity to evaluate the E *vs.* α without the knowledge of the kinetic model. Only the IKP method can lead to the correct kinetic triplet without discrimination of the conversion function from a pre-established set. In this work we present the results obtained at the kinetic analysis of PVC decomposition. We will show that the non-inclusion in the pre-established set of the function of conversion characteristic to the investigated system will lead through the use of Diefallah's composite integral method to an incorrect kinetic triplet.

Applications

Dehydration of calcium oxalate monohydrate

The TG curves corresponding to the dehydration of $CaC_2O_4{\cdot}H_2O$ at the heating rates of 0.987; 2.353; 4.988 and 9.573 K min^{-1} were reported in a previous paper [21]. Using isoconversional differential methods, it was shown [5] that the activation energy decreases from 130 kJ mol^{-1} (for α=0.1) to 63 kJ mol^{-1} (for α=0.9).

Table 1 lists the different kinetic model functions used in this work for applying Diefallah's composite integral method.

The values of the activation parameters of non-isothermal dehydration of $CaC_2O_4{\cdot}H_2O$ corresponding to the considered kinetic models are given in Table 2. The inspection of this Table shows that the kinetic of the investigated reaction is best described by the first order model (F1). The obtained kinetic triplet was used for working the curves α *vs.* T and $\frac{d\alpha}{dT}$ *vs.* T. Figure 1 shows these curves calculated for β=0.987 K min^{-1} in comparison with the corresponding experimental curves. Similar curves were obtained for all heating rates. The calculated values of α exhibit standard deviations higher 10% with respect to the experimental ones for $\alpha\leq0.20$ and $\alpha\geq0.80$. On the other hand, for $0.26\leq\alpha\leq0.90$ the calculated values of $\frac{d\alpha}{dT}$ exhibit standard relative deviations with respect to the experimental ones, which decrease progressively from 10 to –31%. These results show that the kinetic triplet determined by means of the composite integral method does not describe correctly the investigated system. The dependence of E on α, as obtained by isoconversional methods [5], shows that

Table 1 Expressions for $g(\alpha)$ used in this paper

Mechanism	Symbol	$g(\alpha)$
First order kinetic	F1	$-\ln(1-\alpha)$
Random nucleation and growth of nuclei (Avrami-Erofeev equation)	An	$[-\ln(1-\alpha)]^{1/n}$ (n=2; n=3)
Two-dimensional phase boundary reaction	R2	$2[1-(1-\alpha)^{1/2}]$
Three-dimensional phase boundary reaction	R3	$3[1-(1-\alpha)^{1/3}]$
One-dimensional diffusion	D1	α^2
Two-dimensional diffusion (bidimensional particle shape)	D2	$\alpha+(1-\alpha)\ln(1-\alpha)$
Three-dimensional diffusion (Jander equation)	D3	$[1-(1-\alpha)^{1/3}]^2$
Three-dimensional diffusion (Gisling-Braunshtein equation)	D4	$\left(1-\frac{2\alpha}{3}\right)-(1-\alpha)^{2/3}$

Table 2 Activation parameters of non-isothermal dehydration of $CaC_2O_4{\cdot}H_2O$, calculated according to the composite method I (Eq. (3))

Kinetic model	E/ kJ mol^{-1}	$\ln A$/s^{-1}	$-r$
F1	125.6(±2.6)	28.22(±0.71)	0.9926
A2	90.0(±5.7)	18.43(±1.55)	0.9379
A3	78.1(±7.5)	15.14(±2.05)	0.8721
R2	114.9(±2.8)	25.00(±0.76)	0.9901
R3	118.2(±2.6)	26.01(±0.70)	0.9921
D1	153.5(±11.3)	34.10(±3.09)	0.9183
D2	168.4(±8.5)	38.42(±2.30)	0.9597
D3	182.1(±10.4)	40.99(±2.83)	0.9489
D4	172.9(±9.1)	38.26(±2.46)	0.9564

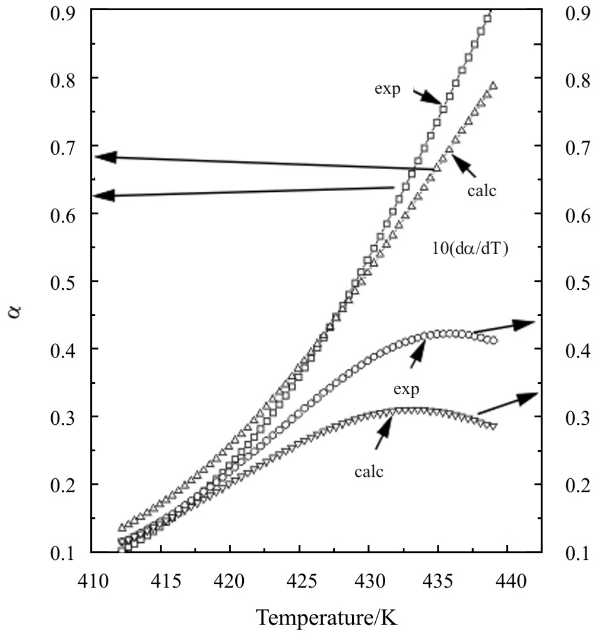

Fig. 1 The curves α *vs*. T and $\frac{d\alpha}{dT}$ *vs*. T for the dehydration of $CaC_2O_4{\cdot}H_2O$. β=0.987 K min^{-1} ; *exp*.=experimental curve; *calc*.=calculated curve using the kinetic triple*t* resulted by means of Diefallah's composite integral method

the dehydration of $CaC_2O_4{\cdot}H_2O$ is a complex process (probably a reversible one), which cannot be described by only one kinetic triplet.

Thermal degradation of PVC

The TG curves corresponding to the thermal degradation of PVC in static air atmosphere at the heating rates of 2, 3, 4, 5 and 10 K min^{-1} were reported in a previous paper [22]. Using these curves and applying isoconversional methods and IKP method, the kinetic parameters of the first degradation process (mainly HCl generation) were evaluated. The obtained results showed that for $0.05 \le \alpha \le 0.70$ the activation energy does not change with the degree of conversion (E=103.2(±2.8) kJ mol^{-1}). For this range of conversion and the kinetic models listed in Table 1 the Diefallah's composite integral method was applied. The obtained results are shown in Table 3.

The inspection of this Table show that the kinetics of the PVC degradation is best described by Avrami-Erofeev random nucleation model (A2) in which the reaction is controlled by initial random nucleation followed by overlapping growth in two dimensions. Nevertheless one has to notice a quite high difference between the value of E corresponding to the model A2 and E evaluated by means of isoconversional methods (E(A2)=86.0 kJ mol^{-1} with respect to E(iso)=103.2 kJ mol^{-1}; $e\% = \frac{E(\text{iso}) - E(\text{A2})}{E(\text{iso})}100 = 16.7\%$). Although the value of $|r|$ corresponding to the model A2 is close to unity, the high difference between E(A2) and E(iso) shows that the kinetic model which describes the investigated change was not considered when the Diefallah's composite integral method was applied.

Table 3 Activation parameters of non-isothermal degradation of PVC, calculated according to the composite method I (Eq. 3)

Kinetic model	E/ kJ mol^{-1}	ln$A$/s^{-1}	$-r$
F1	133.6(±2.1)	23.97(±0.48)	0.9772
A2	86.0(±1.0)	13.20(±0.24)	0.9864
A3	70.1(±2.0)	9.55(±0.46)	0.9304
R2	125.9(±1.6)	22.03(±0.38)	0.9841
R3	128.4(±1.8)	22.66(±0.41)	0.9820
D1	199.3(±6.3)	37.83(±1.45)	0.9161
D2	208.3(±6.9)	39.38(±1.57)	0.9107
D3	218.4(±7.5)	40.38(±1.72)	0.9046
D4	211.7(±7.1)	38.71(±1.62)	0.9087

On the other hand, when the IKP method was applied [23], the result was that the kinetic model A1.5 describes the non-isothermal decomposition of PVC. For this model, using composite integral method (Eq. (3) for all heating rates) one obtains: E(A1.5)=101.9(±0.4) kJ mol^{-1}; ln$A$(s^{-1})=16.81(±0.09) with $|r|$=0.9984. One has to note the good agreement between E(A1.5) and E(iso) as well as the value of $|r|$ substantially higher for model A1.5 than to model A2.

Conclusions

The hypotheses which ground Diefallah's composite integral method for evaluation of the non-isothermal kinetic parameters were discussed. It was pointed out which the use of this method could lead to erroneous results if (a) the activation energy depends on the conversion degree, and (b) the activation energy does not depend on the conversion degree, but the kinetic model describing the investigated change does not belong to the pre-established set. In order to avoid such situations, it is necessary that the application of Diefallah's composite integral method should be preceded by the application of an isoconversional method by means of the dependence of E on α is determined.

References

1 See for example, M. E. Brown, Handbook of Thermal Analysis and Calorimetry, Elsevier, 1998, Vol.1, Ch. 6.
2 S. Vyazovkin and C. A. Wight, Thermochim. Acta, 340 (1999) 53.
3 M. E. Brown, M. Maciejevski, S. Vyazovkin, R. Nomen, J. Sempere, A. K. Burnham, J. Opfermannn, R. Strey, H. L. Anderson, A. Kemmler, R. Keuleers, J. Janssens, H. O. Desseyn, C. R. Li, T. B. Tang, B. Roduit, J. Malek and T. Mitsuhasni, Thermochim. Acta, 355 (2000) 125.
4 P. Budrugeac, D. Homentcovschi and E. Segal, J. Therm. Anal. Cal., 63 (2001) 457.
5 P. Budrugeac and E. Segal, Int. J. Chem. Kin., 33 (2001) 564.
6 P. Budrugeac and E. Segal, J. Therm. Anal. Cal., 72 (2003) 831.
7 K. N. Somasekharan and V. Kalpagam, J. Thermal Anal., 34 (1988) 777.
8 D. Dollimore, The Thermal Analysis – Techniques & Applications (Eds. E. L. Charsley and S. R. Warrington), Royal Society of Chemistry, Cambridge, 1992, p. 31.
9 D. Dollimore, T. A. Evans, Y. F. Lee and F. W. Wilburn, in 'Proc. 19th North Amer. Thermal Anal. Soc.' (Ed. I. R. Harrison), 1990, p. 397.
10 J. Malek, Thermochim. Acta, 200 (1992) 257.
11 P. Budrugeac, A. L. Petre and E. Segal, J. Thermal Anal., 47 (1996) 123.
12 F. J. Gotor, M. Marcias, A. Ortega and J. M. Criado, Int. J. Chem. Kin., 30 (1998) 647.
13 L. A. Perez-Maqueda, J. M. Criado, F. J. Gotor and J. Malek, J. Phys. Chem., 106 (2002) 2862.
14 El-H. M. Diefallah, Thermochim. Acta, 202 (1992) 1.
15 A. I. Lesnikovich and S. V. Levchik, J. Thermal Anal., 27 (1983) 83.
16 A. I. Lesnikovich and S. V. Levchik, J. Thermal Anal., 30 (1985) 667.
17 A. W. Coats and J. P. Redfern, Nature, 20 (1964) 68.
18 C. D. Doyle, J. Appl. Polym. Sci., 5 (1961) 285.
19 M. A. Gabal, Thermochim. Acta, 402 (2003) 199.
20 M. A. Gabal, Thermochim. Acta, 412 (2004) 55.
21 E. Urbanovici and E. Segal, Thermochim. Acta, 107 (1986) 339.
22 A. L. Petre, P. Budrugeac and E. Segal, Rev. Roumaine Chim., 42 (1997) 753.
23 P. Budrugeac, E. Segal, L. A. Perez-Maqueda and J. M. Criado, Polym. Degrad. Stab., 84 (2004) 311.

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