The Application of Isoconversional Methods for Analyzing Isokinetic Relationships Occurring at Thermal Decomposition of Solids

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The thermal decomposition of solids is usually a multistep process. The traditionally applied thermal analysis methods do not measure actual concentrations but rather the extent of substance conversion as a function of temperature. The kinetic processing of such experimental data by the overall method which assumes that the process is a one-step reaction leads to incorrect values of the Arrhenius parameters and to false isokinetic relationships. This can be avoided by using isoconversional methods to compute the effective Arrhenius parameters as a function of the extent of conversion. It was shown that the dependence both of the isokinetic temperature and of its confidence interval on the extent of conversion can be used to detect real isokinetic relationships for multistep processes. The procedure was tested on experimental data and the resulting isokinetic relationship was interpreted in terms of the reaction mechanism. © 1995 Academic Press, Inc.

INTRODUCTION

An isokinetic relationship (IKR) refers to the intersection point of the Arrhenius lines (i.e., ln k versus $1/T$) of a series of reactions defining an isokinetic rate constant (k_{iso}) at an isokinetic temperature (T_{iso}). It has been shown that a strongly proven IKR can be used as an efficient tool for understanding reaction mechanisms; it has been applied successfully to many reactions in both gas and condensed (homo- and heterogeneous) phases (1, 2). The existence of an IKR implies that only one reaction mechanism is followed by all members of the reaction series (3, 4), i.e., all reactions have analogous reaction profiles. In the case where some reactions of a similar series do not meet the IKR condition or more than one IKR occurs, one can conclude that there are differing reaction mechanisms (5–8).

All of these results were obtained under isothermal conditions where the chemical affinity is the only driving

force of a process. However, the kinetics of the thermal decomposition of solids has most often been investigated under nonisothermal conditions. Thermal analysis methods (i.e., differential scanning calorimetry (DSC), differential thermal analysis (DTA), and thermogravimetry (TG)) which measure an extensive property of a system are traditionally used for these purposes (9, 10). Such measurements normally allow no separation of the contributions of single reactions to a change of a physical property. This means that classical problems of detailed solid-state kinetics (11, 12) of primary processes such as nucleation, nuclei growth, and diffusion are beyond the scope of thermal analysis methods. However, this does not mean that they may be ignored in the kinetic processing of experimental data obtained by these methods. A method for the kinetic processing of thermal analysis data should assume that a limiting step (and the associated Arrhenius parameters) may change during the thermal decomposition of a solid. Nevertheless, most popular methods (9, 10) yield one pair of Arrhenius parameters for the whole process of thermal decomposition, treating it as a one-step reaction. That this assumption falls short of reality is shown by the absence of any relationship between the calculated Arrhenius parameters and the actual activation parameters of the reactions composing the process. In the case of nonisothermal processes this is probably the main reason that an artificial IKR (13) is obtained which can disguise the existence of a real one (14).

Therefore, the first problem in calculation of Arrhenius parameters suitable for IKR analysis is the validity of the method applied to the kinetic processing of data on thermal decomposition. It has been shown (15–17) that reliable information about the mechanism and kinetics of complex processes can be obtained by isoconversional methods (also known as Flynn–Wall (18), Ozawa (19), or Friedman (20) methods). One attribute to such methods is that the effective activation energy specific for a given extent of conversion can be determined if several thermal

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analysis experiments are performed at different heating rates. In this way we can estimate the activation energy of the above-mentioned primary processes provided that in some interval of the conversion these processes cause the major contribution to the change in a physical property measured by thermal analysis methods.

The results of isoconversional calculations are presented in terms of the activation energy as a function of the extent of conversion. The shape of this dependence guides the interpretation of the mechanism of a process (21). Not only the activation energy but the preexponential factor can also be estimated (22) for single reactions composing the process. The resulting Arrhenius parameters are governed by the activation energies of the separate reactions as well as by the contributions of these reactions to the overall process rate at a given extent of conversion. Obviously, if one of the reactions composing the process reveals a true IKR in a reaction series we can detect it at those extents of conversion where the contribution of this reaction prevails.

In accord with the above model, the aim of this work was to demonstrate the applicability of the isoconversional method for revealing a true IKR to thermal decomposition of solids comprising two consecutive reactions. We have chosen this type of complex process because its kinetic regularities can be applied to widespread solid processes such as chemical reactions complicated by desorption (23) or diffusion (24). It is believed that this model also can be applied to consecutive nucleation and growth processes. The results so obtained are compared with the results of calculation by the overall method (i.e., assuming that the process occurs in a single step).

DATA MODELING

All kinetic regularities are analyzed by modeling DSC curves. The DSC signal characterizes the overall heat release of all reactions proceeding at a given moment. In the case of the simplest consecutive reactions $A \rightarrow P \rightarrow B$ the intensity of the overall heat release is determined by the rates and the thermal effects of the process steps:

$$I(T) = Q_1(dW_A/dt) + Q_2(-dW_B/dt). \qquad [1]$$

Let us assume that the thermal effects Q_1 and Q_2 are the same and are equal to 41.8 kJ/mole. In addition, we accept that the dependence of $I(T)$ on T is the DSC signal we need. The extent of conversion (W) at any temperature is the ratio of the DSC-curve area at that specific temperature to the complete DSC-curve area.

To model the DSC curves one should know the temperature dependence of the rate of disappearance of the original substance and formation of the product, keeping in mind the linear growth of temperature with heating rate,

namely $q = dT/dt$. The kinetics of first-order consecutive reactions are described by the following system of differential equations (25):

$$dW_A/dt = k_1(T)(1 - W_A) \qquad [2a]$$

$$-dW_P/dt = k_1(T)(1 - W_A) - k_2(T)(1 - W_P) \qquad [2b]$$

$$-dW_B/dt = k_2(T)(1 - W_P). \qquad [2c]$$

In accordance with Eq. [2c] the rate at which the product forms is proportional to the conversion of the intermediate. Its conversion can be found at any time and temperature as a solution of Eqs. [2a] and [2b]. We solved them by the Runge–Kutta method of the fourth order (26) for heating rates of 8, 12, and 16 K/min. The initial conditions were $W_{Ao} = 0$, $W_{Po} = 1$. The starting temperature was determined from [2a] as the temperature at which $W_A = 0.0001$.

Three variations of the process were modeled using three cases for each type. For the first type, an IKR exists for the first reaction alone. In the second type, only the second reaction exhibits an IKR. The third type manifests an IKR for both reactions. The cases within a type are particular occurrences of the same process. They can refer, for example, to the thermal decomposition of the same substance with different additives or to the thermal decomposition of the same complex with different ligands. One case differs from others of the same type in the value of the Arrhenius parameters of the reaction revealing an IKR. The parameters of this reaction in every case were selected so that corresponding Arrhenius lines have a common point of intersection at the same isokinetic temperature. The values of the Arrhenius parameters and of the isokinetic temperature (T_{iso}) are shown in Table 1.

KINETIC CALCULATIONS

The value of T_{iso} was estimated through the slope of the regression line

$$\ln Z_i = a + bE_i,$$

where $b = -1/RT_{iso}$, and i refers to the Arrhenius parameters (the activation energy, E, and the preexponent, Z) found for a select case of the process of the same type. The confidence interval for T_{iso} was determined through the confidence interval for b in the above equation as

$$|\Delta T_{iso}| = |\Delta b|/(Rb^2).$$

The Arrhenius parameters were calculated by both the overall and the isoconversional method. For the overall calculations the logarithmic form of the basic equation of

TABLE 1
The Values of the Arrhenius Parameters and the Isokinetic Temperature
for Three Types of the Consecutive Reactions A → P → B

		A → P			P → B		
Type	Case	E (kJ/Mole)	ln($Z \cdot$ min)	T_{iso} (K)	E (kJ/Mole)	ln($Z \cdot$ min)	T_{iso} (K)
1	1	104.5	27.52		167.2	41.91	
	2	125.4	32.93	465	167.2	41.91	—
	3	146.3	38.34		167.2	41.91	
2	1	125.4	32.93		146.3	36.62	
	2	125.4	32.93	—	167.2	41.91	475
	3	125.4	32.93		188.1	47.21	
3	1	104.5	27.52		146.3	36.62	
	2	125.4	32.93	465	167.2	41.91	475
	3	146.3	38.34		188.1	47.21	

nonisothermal kinetics,

$$\ln[(dW/dT)q/f(W)] = \ln Z - E/RT,$$

was used. It was assumed that the process under study can be described by the model of a first-order reaction, i.e., $f(W) = 1 - W$. This method gives one pair of Arrhenius parameters for all processes at every heating rate.

The isoconversional calculations were performed by means of KinTool software as described in (27). In accordance with the isoconversional method the Arrhenius parameters are estimated from the parameters of the linear dependence $\ln(q/T_W^2)$ on $1/T_W$, where T_W is the temperature corresponding to the same extent of conversion at different heating rates.

DISCUSSION

The results of the Arrhenius parameters and T_{iso} calculations for all of the above-mentioned processes are presented in Tables 2–4. It should be mentioned that in all

cases the activation energy values calculated by the overall method are 10–20 kJ/mole less than the true ones for the first reaction (see Table 1), indicating that in the best case the obtained values can be interpreted as estimates for the activation energies of the first reaction. However, it is evident that these values have no relation to the activation energies of the second reaction. In other words, the overall method gives misleading values for the activation energy of complex reactions.

In all cases the isoconversional method gives activation energy values that reflect the actual kinetics of the complex process. At the beginning ($W = 0.1$), where the first reaction proceeds faster than the second reaction, we obtain the activation energy values for the first reaction. At the final stage ($W = 0.9$), where the second reaction prevails, the calculated values of the activation energy correspond to the activation energies of the second reaction. The deviation of the calculated values from the true ones does not exceed 2 kJ/mole for the first reaction and 7 kJ/mole for the second.

For the process of the first type (Table 2) the overall method gives different values of T_{iso} at different heating

TABLE 2
Values of the Arrhenius Parameters and the Isokinetic Temperature Calculated by the Different Methods for the Process of Type 1

	E (kJ/mole), ln($Z \cdot$ min)								
	Isoconventional method: (W)						Overall method: q (K/min)		
Case	0.1		0.5		0.9		8	12	16
1	104.7	26.30	123.7	31.49	161.3	41.52	93.1 23.38	96.4 24.37	98.7 25.04
2	123.8	31.21	137.4	34.88	162.6	41.71	109.4 28.25	111.7 28.25	113.4 28.76
3	144.8	36.60	152.2	38.57	164.1	41.76	124.0 31.27	125.2 31.66	126.1 31.95
T_{iso} (K)	469 ± 5		484 ± 10		1818 ± 911		471 ± 18	475 ± 8	477 ± 9

TABLE 3

Values of the Arrhenius Parameters and the Isokinetic Temperature Calculated by the Different Methods for the Process of Type 2

	E (kJ/mole), ln(Z · min)											
	Isoconventional method: W						Overall method: q (K/min)					
Case	0.1		0.5		0.9		8		12		16	
1	124.1	31.30	130.5	33.03	141.2	35.91	108.3	27.25	109.3	27.60	126.8	27.89
2	123.8	31.21	137.4	34.88	162.6	41.71	109.4	27.57	111.7	28.25	113.4	28.76
3	123.2	31.06	144.4	36.79	181.7	46.87	110.2	27.77	113.3	28.71	115.7	29.41
T_{iso} (K)	451 ± 175		446 ± 6		445 ± 3		453 ± 54		439 ± 4		365 ± 1952	

rates. Only one of these values (471 ± 18 K), calculated from the data modeled for the heating rate of 8 K/min, corresponds to the true value of T_{iso}. Henceforth, "true" refers to values used when modeling data (see Table 1). The value of T_{iso} found by the isoconversional method for the beginning stage of the process corresponds to the true value of T_{iso}. This value, as can be seen from Fig. 1, grows rapidly with increasing extent of conversion, which is associated with a change in the step limiting the rate at which the process proceeds to the second reaction for which an IKR cannot be established because of equality of the Arrhenius parameters (Table 1).

For the process of the second type (Table 3) the overall method gives basically different values of T_{iso} at different heating rates. None of the calculated values corresponds to the true value of T_{iso}. The value of T_{iso} (445 ± 3 K) estimated by the isoconversional method for the final stage of the process also does not correspond to the true value of T_{iso}. This is probably due to the fact that the deviation of the calculated activation energies from the actual ones for the second reaction is three to four times larger than that for the first reaction. But we can see from Fig. 2 that shifting T_{iso} with decreasing extent of conversion leads to changing the step limiting the process rate from the reaction not resulting in an IKR to the second reaction resulting in an IKR.

For the process of the third type (Table 4) the overall method yields almost equal values of T_{iso} at different heat-

ing rates. The obtained value is a mean between the true values of T_{iso} (465 and 475 K). The values of T_{iso} estimated by the isoconversional method for both the initial and the final stages of the process agree with the true values for the first and second reactions. Figure 3 shows the dependence of the T_{iso} value on the extent of conversion, demonstrating that the step limiting the process rate changes from the first reaction with T_{iso} = 465 K to the second one with T_{iso} = 475 K.

In Fig. 4 the dependences of the confidence interval value for T_{iso} on the extent of conversion are presented. For the first process we can see that such a dependence begins from the flat part ($W < 0.4$) for which the confidence interval value does not exceed 10 K. Evidently this part corresponds to an area with existing IKR. Furthermore, the confidence interval value increases sharply, pointing to "destroying" in IKR at the high extent of the process. For the second process the shape of such a dependence is opposite to the former one. We observe here a changing confidence interval for T_{iso} from the large values at the beginning stage to small values at the final stage. In other words, this dependence discloses a "rising" IKR. The dependence for the third process demonstrates a slight increase in the T_{iso} confidence interval, induced by the lower certainty of estimating the activation energies for the second reaction. It is clear that a small confidence interval for T_{iso} over the entire range of extent of conversion points to the reactions prevailing at different

TABLE 4

Values of the Arrhenius Parameters and the Isokinetic Temperature Calculated by the Different Methods for the Process of Type 3

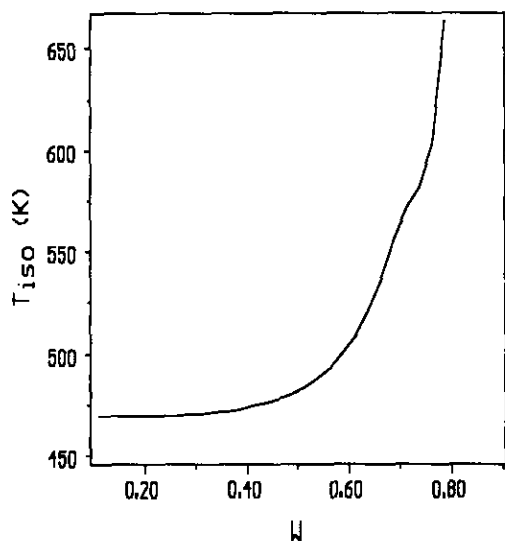|	E (kJ/mole), ln(Z · min)											
	Isoconventional method: W						Overall method: q (K/min)					
Case	0.1		0.5		0.9		8		12		16	
1	105.0	26.37	116.4	29.49	139.2	35.71	92.6	23.24	95.0	23.98	96.7	24.48
2	123.8	31.21	137.4	34.88	162.6	41.71	109.4	27.57	111.7	28.25	113.4	28.76
3	147.7	37.36	160.0	40.58	184.6	47.24	125.1	31.59	127.7	32.34	129.3	32.83
T_{iso} (K)	468 ± 1		470 ± 11		474 ± 23		469 ± 7		470 ± 3		470 ± 1	

FIG. 1. Dependence of the isokinetic temperature on the extent of conversion for the process of the first type.
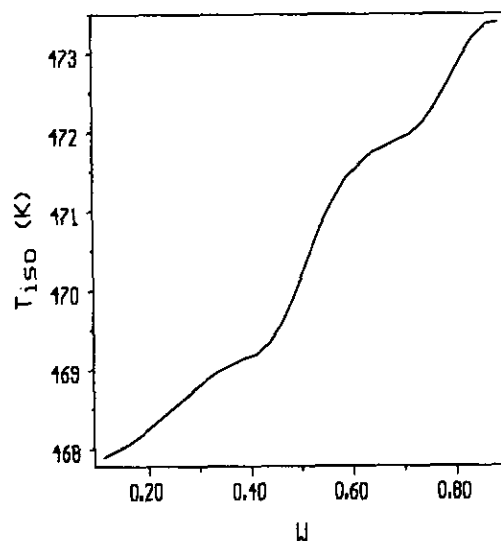

FIG. 3. Dependence of the isokinetic temperature on the extent of conversion for the process of the third type.

stages of the process revealing an IKR. Therefore the shape of the dependence of the confidence interval on the extent of conversion is also related to the existence (or absence) of a true IKR. Thus this property can be applied to its discovery.

EXPERIMENTAL EXAMPLE

As an experimental example we used data (28) on the thermal decomposition of three polyethylene terephthal-

ate (PET) composites namely, (i) pure PET, (ii) PET with 2.4% polyethylene carrier, and (iii) PET with 8% aluminium. Figure 5 displays the dependence of T_{iso} and its confidence interval on the extent of conversion. Within the interval of 30–70% conversion, T_{iso} is almost constant and the confidence interval goes through a minimum. The minimum of the confidence interval value of 10 K is found at $T_{iso} = 622$ K. This value can be interpreted from the point of view of the isokinetic relationship (1, 2) the occurrence of which is explained by a resonant vibrational
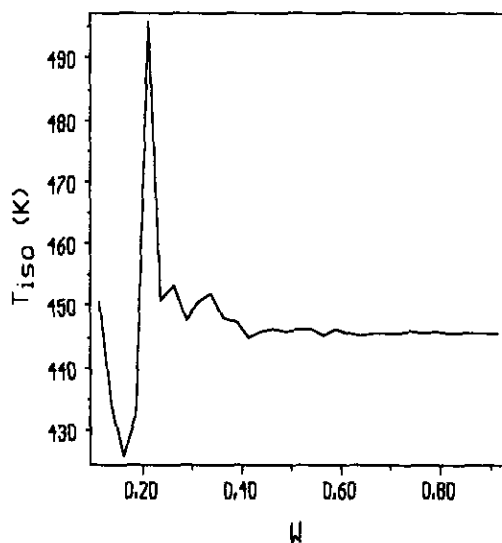

FIG. 2. Dependence of the isokinetic temperature on the extent of conversion for the process of the second type.
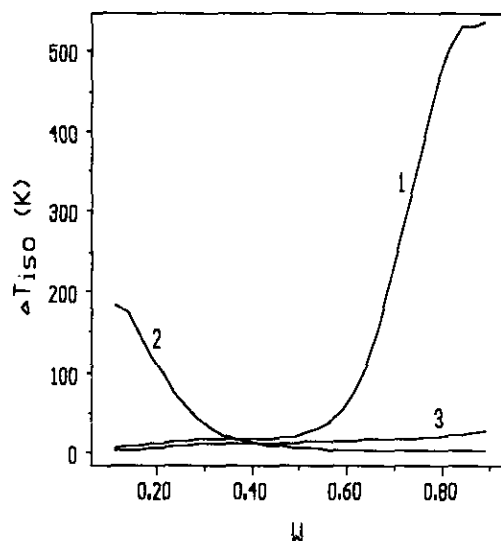

FIG. 4. Dependencies of the confidence interval for the isokinetic temperature on the extent of conversion for the processes of types 1–3.
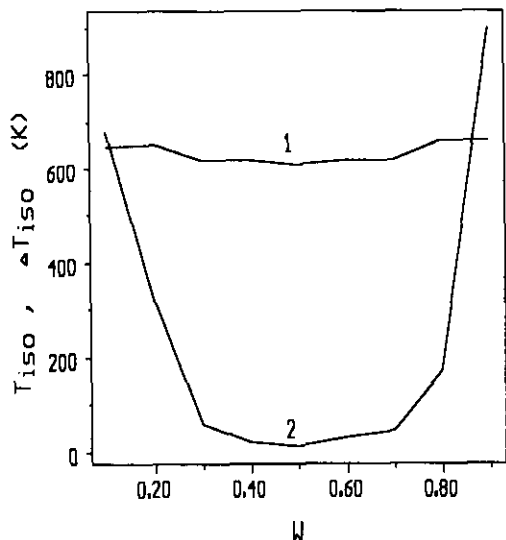
FIG. 5. Dependencies of the isokinetic temperature (Curve 1) and the confidence interval (Curve 2) for it on the extent of conversion for the thermal decomposition of polyethylene terephthalate (PET) composites.

energy exchange between reactants and their molecular environment. The latter is acting as a heat bath providing energy to the reactant to overcome the potential barrier. One result is that the respective resonance vibrational frequency v_{iso} is related to the isokinetic temperature via

$$v_{iso} = k_B \cdot T_{iso}/h,$$

where k_B and h are Boltzman's and Planck's constants, respectively. It has been shown for many isothermal reactions performed in solution or on a catalyst that the above frequency, as required from theory, is actually found in the far-IR spectra of the investigated reaction systems (1, 2).

Accordingly, it is satisfactory to note that the isokinetic temperature of 622 K corresponds to a vibrational frequency of $v_{iso} = 432\,cm^{-1}$, which is in excellent agreement with the experimentally observed far-IR absorption band at 450–430 cm^{-1} (29). This absorption is assigned to a $O-CH_2-CH_2$ deformation vibration in PET. From this we can suppose that the rate-limiting step of PET thermal decomposition is breaking C–O linkages in the polymer chain:
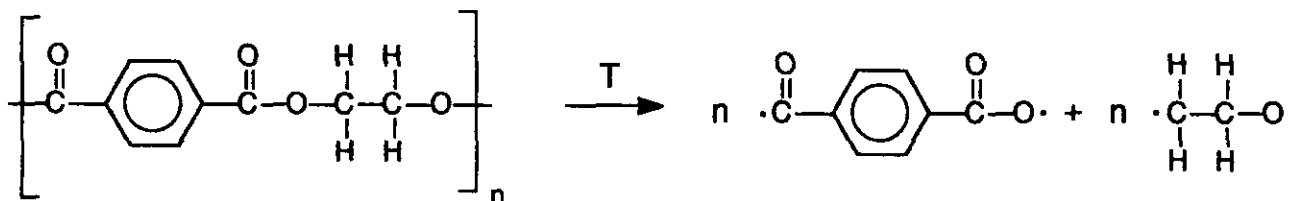
This assumption complies with mass-spectrometer analysis of the gaseous products of PET thermal decomposition (30) in the yield of which 80 mole% of the CH_2CHO constituent was found. The above example shows that the resulting isokinetic relationship is in fact a real one and that it follows the same physical laws as those found for chemically activated isothermal systems.

CONCLUSIONS

Since the overall method of calculating Arrhenius parameters is based on the assumption that a solid state process is a one-step reaction, this method cannot be recommended for revealing the true IKR for processes which always are complex in nature. These methods usually give an artificial IKR. Application of the isoconversional method makes it possible to establish a true IKR at least for those stages of a process where the reaction manifesting it prevails. This can be performed by analyzing the dependence of either a confidence interval for T_{iso} or the T_{iso} value on the extent of conversion. At the same time it should be borne in mind that the T_{iso} value found at a high extent of conversion can diverge substantially from the true one.

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