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Thermally induced reactions of solids: Isokinetic relationships of non-isothermal systems

Sergey Vyazovkin [a] [b] & Wolfgang Linert [a]

[a] Institute for Inorganic Chemistry, Technical University of Vienna,
Getreidemarkt 9, A-1060, Austria

[b] Institute for physical Chemistry, Byelorussian University, Minsk,
Belarus
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Thermally induced reactions of solids: Isokinetic relationships of non-isothermal systems

by SERGEY VYAZOVKIN† and WOLFGANG LINERT*

Institute for Inorganic Chemistry, Technical University of Vienna,
Getreidemarkt 9, A-1060, Austria

Reactions of solids exposed to non-isothermal heating reveal diverse isokinetic relationships (IKR). Some of these effects are exclusively inherent to non-isothermal reactions of solids. The present paper briefly surveys the most commonly encountered IKRs, classifying them into two main types: 'false' and 'true'. The origin of 'false' IKRs, their meaning and their possible practical application, based on the related isokinetic temperatures are elucidated. For 'true' IKRs emphasis is put on the correlation between the experimentally found isokinetic temperature, characteristic bands in infrared spectra, and the mechanism of process. Theoretical considerations are illustrated by experimental examples for reactions of inorganic substances and polymers.

1. Introduction

The general rate equation (1)

$$d\alpha/dt = k(T) f(\alpha), \tag{1}$$

(where α is the extent of conversion, t is time, T is the temperature, $k(T)$ is the rate constant, and $f(\alpha)$ is the reaction model) is used to describe the kinetics of the reactions in solids under isothermal conditions (Brown *et al.* 1980, Sestak 1984). For non-isothermal conditions, when the temperature is varied in time with a constant heating rate ($\beta = dT/dt$), equation (1) takes the following form (Brown *et al.* 1980, Sestak 1984)

$$\beta \, d\alpha/dT = k(T) f(\alpha). \tag{2}$$

Non-isothermal conditions are easily set up in a thermal analysis apparatus for thermogravimetry (TG), derivative thermogravimetry (DTG), differential scanning calorimetry (DSC), etc. In these experiments a change in an extensive property of the reacting system is measured as a function of the temperature. The temperature dependence of the process rate may be described by the Arrhenius equation (3)

$$k(T) = A \exp(-E/RT), \tag{3}$$

(where E (the activation energy) and A (the pre-exponential factor) are Arrhenius parameters). The change in the process rate with the extent of conversion is described by a set of alternative $f(\alpha)$-models (table). These models are based on various theoretical ideas (Sestak 1984) concerning the mechanism of the thermal transformation.

An isokinetic relationship (Lesnikovich and Levchik 1985, Linert and Jameson 1989) (IKR) refers to a common point of intersection of Arrhenius lines (i.e. $\ln k(T)$ against T^{-1}). An ordinate and an abscissa of the point of the intersection define the

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† On leave from: Institute for Physical Chemistry, Byelorussian University, Minsk, Belarus.
* Author for correspondence.

Set of alternative reaction models applied to describe the thermal transformations of solids.

N	Reaction model	$F(\alpha)$	$g(\alpha)$
1	Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
2	Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
3	Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
4	Power law	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
5	One dimensional diffusion	$1/2\alpha^{-1}$	α^2
6	First-order (Mampel)	$1 - \alpha$	$-\ln(a - \alpha)$
7	Avrami-Erofeev	$4(1 - \alpha)[-\ln(1 - \alpha)]^{3/4}$	$[-\ln(1 - \alpha)]^{1/4}$
8	Avrami-Erofeev	$3(1 - \alpha)[-\ln(1 - \alpha)]^{2/3}$	$[-\ln(1 - \alpha)]^{1/3}$
9	Avrami-Erofeev	$2(1 - \alpha)[-\ln(1 - \alpha)]^{1/2}$	$[-\ln(1 - \alpha)]^{1/2}$
10	Three-dimensional diffusion	$3/2(1 - \alpha)^{2/3}[1 - (1 - \alpha)^{1/3}]^{-1}$	$[1 - (1 - \alpha)^{1/3}]^2$
11	Contracting sphere	$3(1 - \alpha)^{2/3}$	$1 - (1 - \alpha)^{1/3}$
12	Contracting cylinder	$2(1 - \alpha)^{1/2}$	$1 - (1 - \alpha)^{1/2}$

logarithm of isokinetic rate constant, $\ln k_{iso}$, and inverse isokinetic temperature, T_{iso}^{-1}, respectively. Beside that, an IKR manifests itself as a correlation between Arrhenius parameters,

$$\ln A_\sigma \approx a + bE_\sigma, \tag{4}$$

where the subscript σ refers to a factor producing a change in Arrhenius parameters.

The nature of the σ factor defines whether an IKR is 'true' (real) or 'false' (artificial). A necessary condition for considering an IKR as a 'true' one is the ability of the σ factor to affect the temperature dependence of the rate of a single-step reaction. If the σ factor is not subject to this condition only a 'false' IKR may occur.

Let us elucidate an overall meaning of T_{iso} which is often used as a characteristic temperature to estimate of the reactivity of solids (Lesnikovich and Levchik 1985). Expression (5)

$$\ln k_{iso} \approx \ln \{[f(\alpha)]^{-1} \beta \, d\alpha/dT\}_\sigma, \tag{5}$$

(here σ takes the values within some interval $[\sigma_1, \sigma_n]$) can be deduced from (2) and (4). This equation allows to define T_{iso} as a temperature at which the right-hand side (r.h.s.) of (5) is least dependent on the factor σ producing a change in Arrhenius parameters. Therefore T_{iso} can be defined as a temperature found from the condition of minima (6)

$$\min \sum_{i<j} \sum \{\ln \{[f(\alpha)]^{-1} \beta \, d\alpha/dT\}_{\sigma i} - \ln\{[f(\alpha)]^{-1} \beta \, d\alpha/dT\}_{\sigma j}\}^2. \tag{6}$$

In practice, the isokinetic temperature is most often evaluated form the parameter b in (4)

$$T_{iso} = (Rb)^{-1}. \tag{7}$$

A confidence interval for this value may be estimated by (8)

$$|\delta T_{iso}| \approx |\delta b|/(Rb^2). \tag{8}$$

The matter of IKRs has been broadly covered in recent reviews (see, e.g. Lesnikovich and Levchik (1985), Linert (1994)) which involve impressive lists of citations. The present paper tries to give further insight into those aspects of both 'false' and 'true'

IKRs that are still not adequately explored. In particular, the origin of commonly encountered 'false' IKRs as well as a meaning (the use) of the related isokinetic temperature will be elucidated. For 'true' IKRs with the mechanism of a process.

2. 'False' IKR

Most often 'false' IKRs arise when varying (i) the reaction model, (ii) conversion, and (iii) the heating rate. Only the first of them is evidently 'false' (artificial) because a change in the reaction model does not influence the kinetics of a process. The two other cases may be misinterpreted as 'true' IKRs.

2.1. *Variation of the reaction model*
Substituting (3) into (2) with ensuing linearization gives (9)

$$\ln[f_j(\alpha)^{-1}\beta \, d\alpha/dT] = \ln A_j - E_j/RT, \tag{9}$$

where j denotes a relation to a given reaction model. This equation as well as its numerous integral approximations underlie the methods of computing Arrhenius parameters (Brown *et al.* 1980, Sestak 1984). The latter are determined by separating the contributions of $k(T)$ and $f(\alpha)$ to the rate of a process. This is usually done fitting the reaction models $f_j(\alpha)$ to the experimental data and selecting (discriminating) the best one. Such a procedure is legitimate only for isothermal kinetics where $f(\alpha)$ and $k(T)$ are experimentally separated ($k(T) = $ const at $T = $ const). The kinetic curve obtained under non-isothermal conditions contains information about $f(\alpha)$ and $k(T)$ in unseparated form. Despite this fact most of the commonly accepted computation methods (Brown *et al.* 1980, Sestak 1984) are based on the above procedure. This evident discrepancy manifests itself as an ambiguity of kinetic description. This means that the rate of a process can be satisfactorily described by (10)

$$\beta \, d\alpha/dT = k_j(T) \, f_j(\alpha), \tag{10}$$

with practically any model $f_j(\alpha)$ and complementary $k_j(T)$ which compensates the error in the choice of a reaction model. The $f_j(\alpha) - k_j(T)$ compensation results in a linear correlation (11)

$$\ln A_j \approx a + bE_j. \tag{11}$$

Therefore, an IKR (11) is inherent to non-isothermal data alone. Evidence of this is available from the article of Li *et al.* (1992) which contains the values of Arrhenius parameters computed by a set of the reaction models for the isothermal and the non-isothermal decompositions of NH_4HSO_4. It is seen from figures 1 and 2 that only Arrhenius parameters derived from non-isothermal data show an IKR.

Liu *et al.* (1992) have experimentally observed an IKR (11) for the thermal decomposition of $Yb(NCS)_3 \cdot 3Glycine \cdot H_2O$ complex study by a TG–DTG and DSC method. Many examples of such an IKR can be composed from Arrhenius parameters reported by Vaimakis (1992) for the thermal decomposition of $La(NO_3)_3 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and their molar mixtures such as required for the formation of the pervoksite series.

An IKR (11) occurs not only in the thermal decomposition but also in reactions of solids synthesis. Logvinenko *et al.* (1992) used the method of quasi-isothermal and quasi-isobaric TG to study the interaction between $Na_3[Rh(NO_2)_6]$ and $H_2C_2O_4 \cdot 2H_2O$ under the helium flow. The Arrhenius parameters computed by the equation of
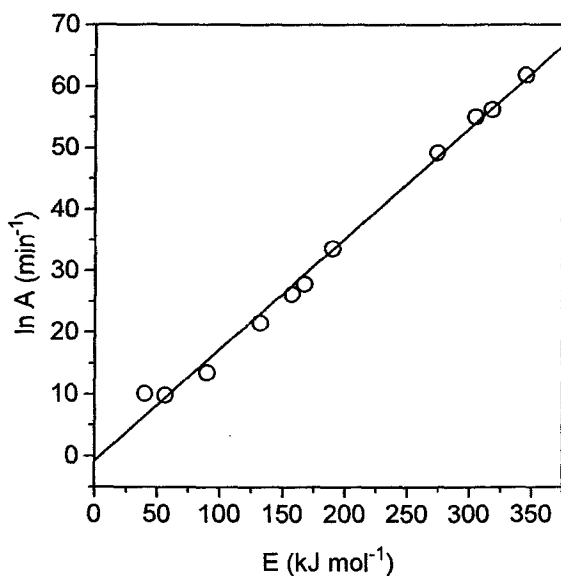
Figure 1. A 'false' IKR (11) for the non-isothermal decomposition of NH_4HSO_4 (Li *et al.* 1992).
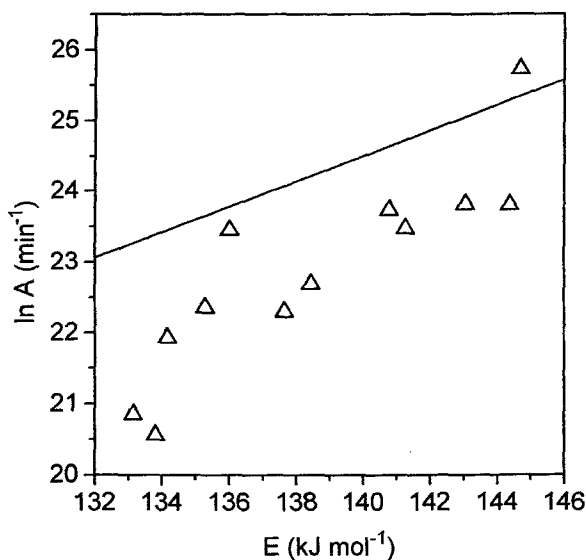
Figure 2. Arrhenius parameters computed by Li *et al.* (1992) with different reaction models for the isothermal decomposition of NH_4HSO_4. The straight line represents the IKR depicted in figure 1.

nucleation $f(\alpha) = (1 - \alpha)[-\ln(1 - \alpha)]^m$ (Avrami–Erofeev equations in the table with $m = 3/4, 2/3, 1/2, 1/3, 1/4$ fit into a straight line $\ln A$ $(\text{min}^{-1}) = -6.285 + 0.301\ E$ (kJ mol^{-1}) with the correlation coefficient 0.99999.

The Arrhenius parameters found by Abd El-Salam *et al.* (1992) for the non-isothermal decomposition of Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} succinate complexes

show no profound IKR when varying the reaction model. However, the method used to compute Arrhenius parameters raises serious doubts about the validity of the reported values. Equation (2) after substitution $k(T)$ (3) can be written in the integral form

$$g(\alpha) = (A/\beta) \int_0^T \exp(-E/RT)\,dT, \qquad (12)$$

where

$$g(\alpha) = \int_0^\alpha [f(\alpha)]^{-1}\,d\alpha$$

is the integral form of a respective reaction model. Integrating (12) Abd El-Salam *et al.* (1992) have induced an oversimplified approximation

$$g(\alpha) \approx (AR/\beta E)\exp(-E/RT).$$

The most proven approximations of (12) set a more complex function of the temperature

$$g(\alpha) \approx (AR/\beta E)\exp(-E/RT)\,T^2\,(1 - 2RT/E)/\{1 - m(RT/E)^2]\},$$

with m within the range 0–6 (Agrawal 1992).

Let us elucidate the meaning of T_{iso} found from (11). Then the reaction model plays the role of the σ factor (see (4)) which produces a change in Arrhenius parameters. In this case, T_{iso} is a temperature at which the logarithm of the rate constants (r.h.s. of (5)) computed by different reaction models $f_j(\alpha)$ is least dependent on j. Then the condition of minima (6) takes the form of (13)

$$\min \sum_{i<j}\sum \{\ln\{[f_i(\alpha)]^{-1}\beta\,d\alpha/dT\} - \ln\{[f_j(\alpha)]^{-1}\beta\,\delta\alpha/dT\}\}^2. \qquad (13)$$

Since both β and $d\alpha/dT$ do not depend on the form of the model $f(\alpha)$, equation (13) can be simplified to (14)

$$\min_{\alpha \in [0,1]} \sum_{i<j}\sum \{\ln[f_i(\alpha)] - \ln[f_j(\alpha)]\}^2. \qquad (14)$$

This allows T_{iso} to be found as a temperature corresponding to the conversion at which the difference between the reaction models used is a minimum. Note, that this value depends on the set of the reaction models used. Specifically for the set of $f(\alpha)$-models presented in the table it results in 0·515 (Vyazovkin and Linert 1994). It follows that the temperature related to this conversion, $T_{0·515}$ (Vyazovkin and Linert 1994). It follows that the temperature related to this conversion, $T_{0·515}$, is an estimate for T_{iso}. Extensive computations on model data (Vyazovkin and Linert 1995 *b*) have confirmed the validity of this estimate. An essential fact is that T_{iso} found from an IKR (11) is a temperature related to a fixed conversion. Because of this it can be used to compare the reactivity of solids.

2.2. *Variation of conversion*

Many examples of an IKR (15)

$$\ln A_\alpha \approx a + bE_\alpha, \qquad (15)$$

(henceforth, the subscript α denotes the values related to a given conversion) can be found in articles of Cooney *et al.* (1984) and MacCallum and Munro (1992). Cooney *et al.* (1984) analysed the kinetics of the thermal oxidative degradation of

untreated and flame-retarded poly(ethylene terephthalate) fabrics using TG in a flowing air atmosphere. MacCallum and Munro (1992) also used TG to study the thermal decomposition of polymer composites. These composites separately included pure polymer, polymer with 2·4% of polyethelene as carrier material, and polymer with 8% aluminium flake as the metal additive. The following polymers were examined: poly(styrene), low and high density poly(ethylene), poly(propylene), nylon 6, poly(ethylene terephthalate), poly(vinyl chloride). Additionally, IKRs (15) can be composed from the Arrhenius parameters reported by Kim *et al.* (1992) for the thermal decompositions of $CaCO_3$ (TG in an air atmosphere) and by Diefallah (1992) for $Mn(CH_2COO)_2$ (TG in a N_2 atmosphere).

All these IKRs have been discovered when employing the isoconversional methods to compute Arrhenius parameters. These methods are applicable if several kinetic curves have been taken at different heating rates. Writing (2) for different heating rates β_i and considering it at a constant conversion leads to (16)

$$\beta_i (d\alpha/dT)_{\alpha, i} = k(T_{\alpha, i})f(\alpha). \tag{16}$$

Equation (16) can be rewritten as (17)

$$\ln [\beta_i (d\alpha/dT)_{\alpha, i}] = \ln [A_\alpha f(\alpha)] - E_\alpha/RT_{a, i}, \tag{17}$$

which is at the basis of the isoconversional method of Friedman (1963). A modification of this method has been used by Kim *et al.* (1992). Integral approximations of (17) are also well-known as the isoconversional methods of Ozawa (1965) and Flynn and Wall (1966). These methods have been employed by Cooney *et al.* (1984) and Diefallah (1992).The specificity of the isoconversional methods is that they reveal a dependence of the activation energy upon the conversion, i.e. E_α on α, in the case of complex (multistep) processes (see Vyazovkin and Lesnikovich (1990)). In particular, a dependency of E_α ov α was observed by Cooney *et al.* (1984), MacCallum and Munro (1992), Kim *et al.* (1992), and Diefallah (1992) in all the cases when an IKR (15) occurs. In (15), conversion plays the role of the σ factor (see (4)) with the variation of which Arrhenius parameters are changed. T_{iso} is a temperature at which the logarithm of the rate constants (r.h.s. of (5)) evaluated at different heating rates is least dependent on α. The condition of minima (6) takes the form of (18)

$$\min \sum_{i<j} \sum \{\ln \{[f(\alpha_i)]^{-1}\beta_i (d\alpha/dT)_i\} - \ln \{[f(\alpha_j)]^{-1}\beta_j (d\alpha/dT)_j\}\}^2. \tag{18}$$

This expression gives zero at any T because it is a difference of logarithms of the rate constants at the same temperature. In other words, T_{iso} is an arbitrary temperature from the experimental interval.

Vyazovkin and Linert (1995 b) have established that an IKR (15) takes place independently of the reaction model substituted in the intercept $\ln [A_\alpha f(\alpha)]$ to isolate the dependence of $\ln A_\alpha$ on α. The value of T_{iso} critically depends on the reaction model used for the substitution. However, when a correct reaction model has been substituted, the T_{iso} values lie within the region of the experimental temperatures (Vyazovkin and Linert 1995 b). Nevertheless, for complex kinetics irrepresentable in the form with separable variables (1), no single $f(\alpha)$ model can be considered as a correct one. Thus T_{iso} computed from an IKR (15) may materially deviate from the region of the experimental temperatures.

In particular, the isokinetic temperatures evaluated from the IKRs reported by Cooney *et al.* (1984), and MacCallum and Munro (1992) exceed 1000 K, i.e. they lie

remarkably higher than the temperature region of the thermal degradation of the examined polymers. This implies that these T_{iso} values are probably not valid and cannot be used to recognise a change in the kinetics of the thermal degradation, as it was attempted by Cooney *et al.* (1984). In contrast, the T_{iso} values which may be computed from the Arrhenius parameters of the thermal decomposition of $CaCO_3$ ($T_{iso} = 933$ K) and $Mn(CH_2COO)_2$ ($T_{iso} = 562$ K) fit into respective intervals of the decomposition 900–1060 K (see Kim *et al.* (1992)) and 510–610 K (see Diefallah 1992).

2.3. *Variation of the heating rate*

When Arrhenius parameters are computed for a fixed $f_j(\alpha)$ but different heating rates, β, an IKR (19) may be observed

$$\ln A_\beta \approx a + bE_\beta, \qquad (19)$$

here the subscript β indicates a relation to a given heating rate. Tanaka and Koga (1988) have observed such an IKR for the thermal dehydration $K_2CuCl_4 \cdot 2H_2O$. Koga and Tanaka (1991) attempted to analyse theoretically this IKR using a modelled single-step reaction which changes Arrhenius parameters but retains the reaction model when varying heating rate. Analogously to an IKR (15) it has been found (Koga and Tanaka 1991) that an IKR (19) manifests itself independently of the particular form of the reaction model used to compute Arrhenius parameters. However, the parameters of (19) depend on the reaction model. Tanaka and Koga (1988), Koga and Tanaka (1991) are inclined to consider an IKR (15) as a 'true' one provided a valid reaction model was identified for the reaction. With respect to the model process they used, such a conclusion cannot be drawn for an actual process (see Tanaka and Koga (1988)) until it is proven that the process being studied is not a multistep reaction. As was mentioned, such a reaction reveals a dependence of the activation energy on conversion if the isoconversional method is used for kinetic computations (Vyazovkin and Lesnikovich 1990). A dependence of E_α on α has been actually revealed by Tanaka and Koga (1988) for the thermal dehydration of $K_2CuCl_4 \cdot 2H_2O$.

For a single-step reaction (a reaction which retains E, A, $f(\alpha)$ when varying β), a changes in the heating rate induces no remarkable change in the values of Arrhenius parameters whatever reaction model was used for the computations (see Vyazovkin and Linert (1995 *b*)). Thus an IKR (19) cannot be observed for a single-step reaction.

In the general case, an IKR found in the form (19) should be considered as a 'false' one. To understand its origin, the fact that it was detected for a multistep reaction should be taken into account. In this situation, computed Arrhenius parameters describe the process of the overall conversion of a substance. Their values are determined by the Arrhenius parameters of single reactions as well as by the contributions of these reactions to the overall conversion. Under different temperatures, different reactions may dominantly contribute to the overall conversion. An increase in the heating rate shifts the temperature region of a reaction towards higher temperatures. This means that the Arrhenius parameters corresponding to data obtained under higher heating rates are determined by those reactions which dominantly contribute to the overall conversion under higher temperatures. Therefore an IKR (19) arises only for a multistep process, whose computed Arrhenius parameters vary because of the change in the temperature region. Noteworthy, the same reason gives rise to an IKR (15). Hence both IKRs (15) and (19) undeniably are 'false' because they are not subject to the change of the temperature dependence of the rate of a single-step reaction.

The common origin of IKRs is also embodied in the similar course of dependencies

of E_α on α and E_β on β. This fact may be experimentally observed (see Tanaka and Koga (1988)) for the thermal dehydration of $K_2CuCl_4 \cdot 2H_2O$.

Let us elucidate a meaning of T_{iso} evaluated from (19). In this equation, the heating rate is the σ-factor (see (4)) which changes Arrhenius parameters. T_{iso} is a temperature at which the logarithm of the rate constants (r.h.s. of (5)) evaluated at the different heating rates is least dependent on β. The condition of minima (6) takes here the same form as (19). This means that T_{iso} for such a case is also an arbitrary temperature from the temperature interval.

If the $f(\alpha)$-model is not properly taken the isokinetic temperature may lie out of the region of the experimental temperatures. For instance, the T_{iso} values evaluated from the b parameters of (19) reported by Tanaka and Koga (1988) exceed 750 K whereas the temperature region of the dehydration is 330–410 K. Note that such a case is a rather common one, as emphasized in the previous section, because for the main part of complex processes no single $f(\alpha)$-model can be assumed as a valid reaction model.

Therefore in general the isokinetic temperature associated with IKRs (15) and (19) cannot be used as an estimate of the reactivity. Furthermore, they both are 'false' because a change in conversion or in the heating rate does not affect Arrhenius parameters of a single-step reaction.

3. 'True' IKR

'True' IKRs may only arise if the σ factor (4) is associated with modification of a reagent or an environment for a series of closely related reactions. A properly established IKR can be used as an efficient tool for understanding reaction mechanisms (Linert 1994). The existence of an IKR implies that only one reaction mechanism is followed by all members of the reaction series, i.e. all reactions have analogous reaction profiles. When reactions of an apparently similar series do not meet the IKR condition (or more than one IKR occurs) differing reaction mechanisms can be concluded.

The occurrence of an IKR has been explained theoretically by Linert and Jameson (1989). An important point for this is the existence of a resonant vibrational energy exchange between reactants and their molecular environment. The latter acts as a heat-bath providing the energy necessary for the reactants to overcome the potential barrier. One of the results from this is that, when an IKR occurs, the resonance vibrational frequency ν_{iso} is related to the isokinetic temperature by (20)

$$\nu_{iso} = k_B T_{iso}/h, \tag{20}$$

(where k_B and h are Boltzmann's and Planck's constants respectively). It has been shown for many isothermal reactions performed in solution or on catalyst surfaces that this frequency is to be found in the far infrared spectra of the investigated reaction systems (Linert and Jameson 1989). In turn this means that a reliable evaluation of the isokinetic temperature helps to elucidate the reaction pathway, for example the transformation of a specific reaction group.

3.1. Problems and methods to compute IKRs

Establishing 'true' IKRs is of considerable interest as applied to the reactions of solids. But here a problem, specific to the thermal analysis measurements, arises. These measurements normally allow no separation of the contributions of single reactions to a change in a physical property. Because of this detailed solid-state kinetics of primary processes such as nucleation, nuclei growth, and diffusion are beyond the scope of

thermal analysis technique. Clearly the existence of these processes may not be ignored in kinetic processing of experimental data. A method of kinetic processing of thermal analysis data should assume that a limiting step (and associated Arrhenius parameters) may change during a process. Nevertheless, most popular (discriminating) methods (see Brown *et al.* (1980), Sestak (1984)) yield one pair of Arrhenius parameters for the whole process, treating it as a single-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 making up the process.

The problem mentioned above is additionally burdened by the ambiguity of evaluating Arrhenius parameters even for a single-step process. Arrhenius parameters are evaluated by discriminating among alternative reaction models which usually are equivalent descriptions of a process (see equation (10)). This procedure results in a set of statistically equivalent Arrhenius parameters which, however, crucially differ in their numerical values. Vyazovkin and Linert (1994) have shown with model data that such ambiguity may lead to the remarkable uncertainty in estimating T_{iso}. These problems are the main impediment to reliably detect IKRs occurring in solids under non-isothermal conditions.

However, Vyazovkin and Linert (1994) have shown that Arrhenius parameters acceptable for IKR analysis can be computed by isoconversional methods. These methods are non-discriminating and applicable for multistep processes. By the isoconversional methods we can estimate the activation energy of the primary processes, provided that in some interval of conversions this process dominantly contributes to a change in a measured physical property. Obviously, if one of the reactions composing the process reveals a 'true' IKR in a reaction series we have a chance to detect it at those conversions where the contribution of this reaction prevails.

The main problem that constrains the isoconversional methods from computing a 'true' IKR is ambiguously estimating the pre-exponential factor from the $\ln [A_\alpha f(\alpha)]$ (17). An unambiguous value of $\ln A_\alpha$ can be estimated via an artificial IKR (15). After determination of a and b in (15) the E_α value found from (17) is substituted in (15) to estimate $\ln A_\alpha$. The validity of this procedure has been proven by Vyazovkin and Linert (1955 b). When Arrhenius parameters have been known, the parameters of a 'true' IKR are available from (21)

$$\ln A_{\alpha, i} \approx a_\alpha + b_\alpha E_{\alpha, i} \qquad (21)$$

(where *i* refers to a given reaction of the reaction series). In accord with (21), for a single reaction series one may compute as many IKRs as the number of conversions used to evaluate Arrhenius parameters. Note, if E_α depends on α (multistep process), then both T_{iso} and $|\delta T_{iso}|$ estimated by (7) and (8), respectively, will also depend on α. The potentialities of the isoconversional method to detect an IKR for complex processes are examined by Vyazovkin and Linert (1995 a).

3.2. *Experimental examples*

The above-mentioned data of MacCallum and Munro (1992) on the thermal decomposition of polymer composites with poly(ethylene terephthalate) as a basis polymer has been analysed by Vyazovkin and Linert (1995 a) with the aim to detect a 'true' IKR. Figure 3 displays the dependence of T_{iso} and its confidence interval on the extent of conversion. At $\alpha = 0\cdot3$–$0\cdot7$ T_{iso} is almost constant. The $|\delta T_{iso}|$ has its minimum
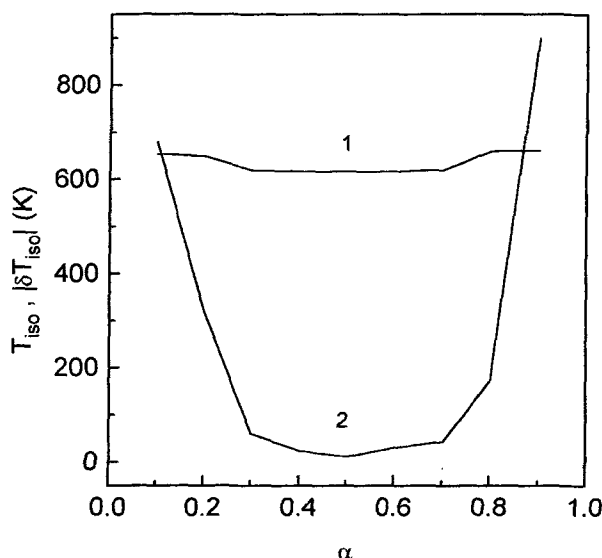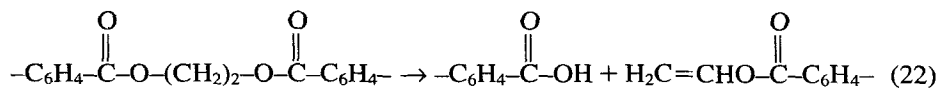
Figure 3. Dependence of the isokinetic temperature and its confidence interval on the extent of conversion for the thermal decomposition of poly(ethylene terephthalate) composites (MacCallum and Munro 1992).

of 10 K at $\alpha = 0.5$ which corresponds to $T_{iso} = 618$ K. The latter value gives by (20) $v_{iso} = 430$ cm^{-1}. This vibrational frequency matches the infrared absorption band (450–430 cm^{-1}) assigned by Siesler and Holland-Moritz (1980) to a O–CH$_2$–CH$_2$ deformation vibration in poly(ethylene terephthalate). From this we can derive that breaking C–O linkages in the polymer chain (22) seems to limit the rate of the thermal decomposition of the considered polymer composites.

$$-C_6H_4-\overset{\overset{\displaystyle O}{\|}}{C}-O-(CH_2)_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_4- \rightarrow -C_6H_4-\overset{\overset{\displaystyle O}{\|}}{C}-OH + H_2C=CHO-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_4- \quad (22)$$

Also the thermal decomposition of poly(ethylene terephthalate) in the form of untreated and flame-retarded fabrics with different composition has been examined by Cooney et al. (1984) using TG in air. From the dependence of E_a on α computed by the isoconversional method the authors have discerned three stages and estimated averaged Arrhenius parameters for each of them. It is seen from figure 4 that Arrhenius parameters for all three stages of the thermal decomposition of the examined specimens comply with an IKR condition. It is satisfactory to note that corresponding values of $T_{iso} = 635$ K and $v_{iso} = 441$ cm^{-1} are in agreement with the preceding results.

Gupta and Jais (1993) have studied the kinetics of the thermal decomposition of Nylon-6 composites by TG in the presence of static air. Specimens contained a mixture of five parts of Nylon-6 with one part of a metal oxide. Altogether 15 different mixtures have been analysed. Arrhenius parameters were computed by the discriminating method and are reported (see Gupta and Jais (1993)) to meet an IKR condition with $T_{iso} = 842$ K. With regard to (20) this value gives $v_{iso} = 585$ cm^{-1} which approaches a frequency 580 cm^{-1} characteristic of C=O vibrations in amide group of nylon-6
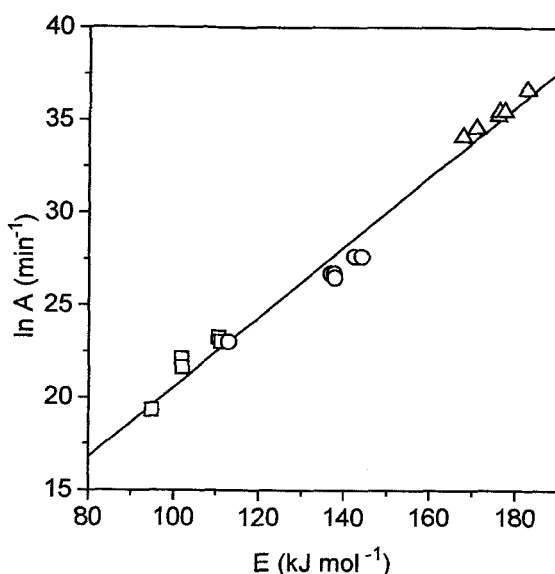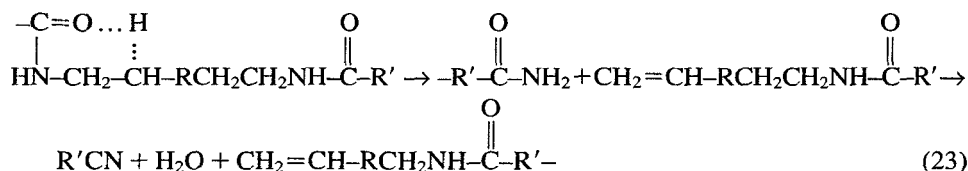
Figure 4. IKR composed from Arrhenius parameters reported by Cooney *et al* (1984) for the thermal degradation of poly(ethylene terephthlate) fibres (squares: stage 1; triangles: stage 2; circles: stage 3).

(see Siesler and Holland-Moritz (1980)). This group plays a leading part in the thermal degradation of polyamides (23) (see Encyclopedia of polymer science and engineering (1985)).

$$-C\!=\!O\ldots H \qquad\qquad O \qquad\qquad O \qquad\qquad\qquad\qquad O$$

$$\underset{|}{\text{HN--CH}_2\text{--CH--RCH}_2\text{CH}_2\text{NH--}\overset{\|}{\text{C--R}'}} \rightarrow -\text{R}'\!-\!\overset{\|}{\text{C}}\!-\!\text{NH}_2 + \text{CH}_2\!=\!\text{CH--RCH}_2\text{CH}_2\text{NH--}\overset{\|}{\text{C--R}'} \rightarrow$$

$$O$$
$$\|$$

$$\text{R}'\text{CN} + \text{H}_2\text{O} + \text{CH}_2\!=\!\text{CH--RCH}_2\text{NH--}\overset{\|}{\text{C--R}'}\!-\! \qquad\qquad\qquad (23)$$

Fairbridge *et al.* (1978) have found that Arrhenius parameters for cellulose pyrolysis as well as a number of wood products follow to equation

$$\ln A(\min^{-1}) = -1 \cdot 86 + 0 \cdot 2 E(\text{kJ mol}^{-1}), \qquad\qquad (24)$$

to which the following values of $T_{iso} = 602\,\text{K}$ and $\nu_{iso} = 418\,\text{cm}^{-1}$ correspond. In connection with these results it is pertinent to mention the studies of Fernandez *et al.* (1990 *a, b*) performed on cellulose fibres. Fernandez *et al.* (1990 *a, b*) computed by (17) Arrhenius parameters for the thermal degradation of cotton grafted with vinyl and methyl acrylate (see Fernandez *et al.* (1990 *a*)) as well as their binary mixtures (see Fernandez *et al.* (1990 *b*)). Figure 5 shows an IKR for the studied process. The straight line of the IKR has a slope $b = 0 \cdot 1943$ which is virtually equal to that of (24). The values of T_{iso} and ν_{iso} related to this IKR are 619 K and 439 cm^{-1}, respectively. The far infrared (i.r.) spectra of cellulose discloses a broad absorption band at about 450 cm^{-1}, (see Siesler and Holland-Moritz (1980)). Hummel (1966) assumed that this band is due to the bending vibrations of the OH groups and the glucosidic ether linkages which are strongly coupled. Cleavage of both glucosidic and glycosidic linkages has
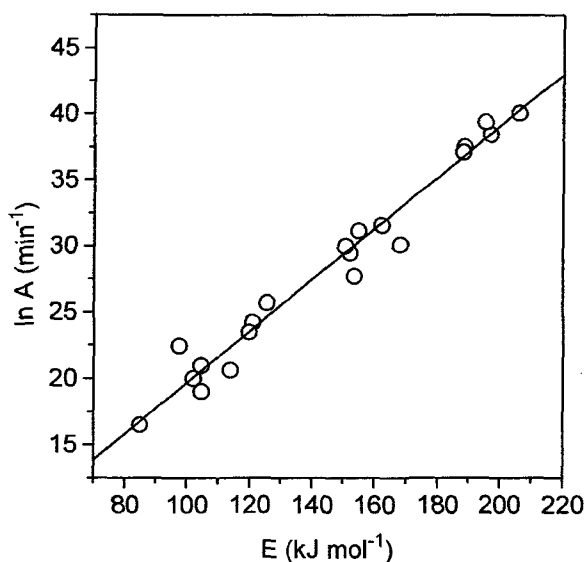
Figure 5.   IKR composed from Arrhenius parameters reported by Fernandez *et al.* (1990a, b) for the thermal degradation of grafted cotton fibres.
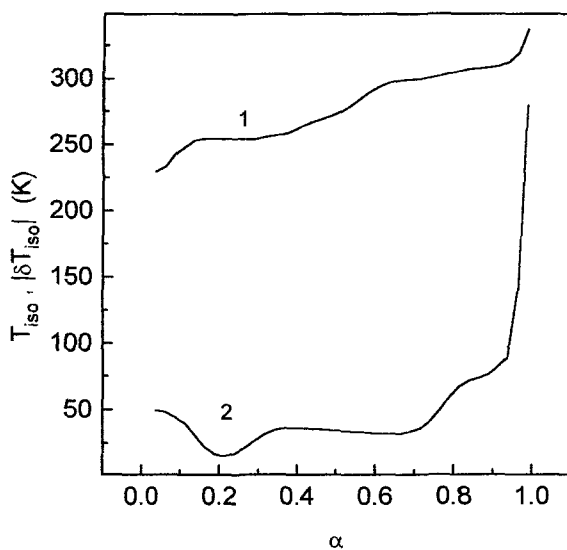

Figure 6.   Dependence of the isokinetic temperature and its confidence interval on the extent of conversion for the thermal decomposition of the tetranuclear complexes $Cu_4OCl_6L_4$ with various ligands (L = piperidine, morpholine, triphenylphosphine oxide).

a dominant role in the thermal degradation of cellulose (see Encyclopedia of polymer science and engineering (1985)). At the early stage (580–620 K) the breakdown of the glycosidic linkages results in the formation of levoglucosan. At higher temperatures the glucosidic linkages are ruptured with the disintegration of the ring.

The thermal decompositions of tetranuclear Cu(II) complexes with the general composition $Cu_4OCl_6L_4$ has been performed by Vyazovkin and Linert (1995 c) by TG

under flowing nitrogen. Complexes with a piperidine (I), morpholine (II) and triphenylphosphine oxide (III) as a ligand (*L*) were studied. It has been assumed that thermolyses of these complexes with different ligands may form a reaction series and reveal 'true' IKRs.

Figure 6 displays the dependencies of T_{iso} upon the extent of conversion. Within the interval of 0·15–0·30 conversions, T_{iso} is almost constant. The confidence interval goes through a minimum of 15 K at $\alpha = 0·2$ which relates to $T_{iso} = 255$ K. The substitution of the latter value into (4) gives a vibrational frequency of $v_{iso} = 177 \pm 10$ cm^{-1}. This value accords well with the experimentally observed far-i.r. absorption bands assigned by Linert *et al.* (1993) to stretching vibration in the trigonal CuCl$_3$ chromophore in the piperidine, morpholine, and triphenylphosphine oxide complexes, respectively. This suggests the CuCl$_3$-group as a possible centre of the reaction, which thus appears to be the rate-limiting step of the thermal decomposition of the complexes at its beginning. The experimental results of Langfelderova *et al.* (1991): the observed change in Cu–Cl vibration (i.r. spectra) at the very early stage of the decomposition and the formation of CuCl (X-ray diffraction) as a decomposition product at late stage, confirm this assumption.

Detecting IKRs is not without appeal, even though i.r. spectra are not in hand. The existence of a single IKR indicates that the members of the series have a common reaction pathway invariant to the factor varied in a reaction series. If due to such a variation some processes drop out of the IKR condition and/or a new IKR forms, the factor which crucially influences the mechanism may be revealed. Muraishi and Yokobayashi (1992) employed TG to investigate the thermal dehydration of lanthanide oxalate, malonate and succinate hydrates as well as the thermal decomposition of their anhydrides. Arrhenius parameters have been computed by the discriminating method. Muraishi and Yokobayashi (1992) discovered that the variation of the cation in each of these substances gives rise to an IKR. Noteworthy is that in most of the detected IKRs the increase of the values of Arrhenius parameters is in inverse proportion to the increase of the molecular weights of the lanthanides. This undeniably points to physical reasons underlying the effect. Of special interest is that the light (La, Ce, Pr, Nd, Sm, Eu) and the heavy lanthanides (Gd, Tb, Dy, Er, Tm, Yb, Lu) form two different IKRs in the case of the dehydration. It suggests that each of the two groups of the lanthanide compounds has a common reaction step invariant to the cation. Furthermore the difference in these steps for the light and the heavy lanthanides may also be assumed. Such a conclusion is not applicable to the decomposition of anhydrides which show practically no difference in IKRs for both groups of lanthanides.

The thermal dehydration of single crystal and powdered samples of Li$_2$SO$_4 \cdot$ H$_2$O has been intensively examined by Brown *et al.* (1993). Arrhenius parameters for this process have been derived from isothermal measurements in constant-volume apparatus as well as from TG and DSC in both isothermal and non-isothermal conditions. Similarly to the previous example the *E* and ln *A* values are grouped about two straight lines (see Brown *et al.* (1993)), applicable to single crystals and crushed powder samples. Brown *et al.* (1993) ascribed the occurrence of the observed IKRs to unidentified inconsistencies in measurement methods. However these inconsistencies can scarcely explain the occurrence of two separate IKRs for crystal and powder samples. Hence, the physical grounds behind the effect also should not be rejected. Especially as the influence of the crystals size on the reaction mechanism is well known for solids (see, e.g. Brown *et al.* (1980)). This factor seems to cause a change in the reaction step of the thermal dehydration of Li$_2$SO$_4 \cdot$ H$_2$O.

4. Conclusions

The key to the interpretation of IKRs lies in the nature of the factor which is behind the observable variation in Arrhenius parameters. Only physical factors such as modifying of a reagent or a reaction environment may lead to a 'true' IKR. Detecting 'true' IKRs is very helpful in searching for the actual reaction pathways especially when far i.r. spectra of reagents are available. It also helps to determine the factors crucial to the change of the reaction mechanism. The factors which stay behind 'false' IKRs have mathematical (numerical) nature. Because of this 'false' IKRs cannot be interpreted in terms of the reactions mechanism. However, some profit can be gained even in this case. For instance the value of the isokinetic temperature can be used in estimating the thermal stability of a substance (variation of the reaction model) or in verifying the validity of the reaction model (variation of the heating rate and conversion).

Acknowledgment

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