Special Review

DIFFERENT KINETIC EQUATIONS ANALYSIS

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A software is described enabling kinetic analysis under non-isothermal or isothermal conditions from DSC, or from TG data. The program offers thirteen methods of kinetic analysis for DSC, three for isothermal analysis and two for TG, with eight different functions for the choice of the proper mechanism for each of them.

Introduction

In view of the numerous limitations seen in the computer system used at the time of our first experiment on solid-solid transitions, and more especially of solid-plastic transitions [1], our study was principally centred on the kinetic characterization of those transitions, with the help of Freeman-Carroll, Kissinger and Ozawa's methods. This study allows the conception and the restatement of a computation system, much more complete, better applied to the characterization of the phenomena taking place at the solid state, and, more generally, able to permit the study of a great number of physico-chemical processes. Thanks to a particular interfacing system, it is possible to convey acquisition data obtained with the HP 86 calculator of our differential scanning calorimeter, to treat them on a 386 AT microcomputer. The superiority of this system is that it offers no limitation, is able to deal with the totality of recorded points, makes it possible to extend calculations up to the quantity of the kinetic model required for the study of the phenomenon, and, through the interfacing system's flexibility, is able to treat,

with the same kinetic equations, data sprung from a differential scanning analysis or from an isothermal analysis, as well as thermodynamic data, from three sub-programs (KIN, KINISO and TGA). The integration limits of the thermograms which can be kept when determined, all the kinetic calculations are relating to the same value of the transition enthalpy (ΔH_{Tr}), this allows the comparisons between the different methods. The software which permits to plot the Arrhenius lines (for each kinetic exponent value) makes easier the selection of the interval which gives a linearization of the Arrhenius equation. The preceding study in solid-plastic transition [1] showed that the kinetic homogeneous law, applied to Freeman-Carroll's method, is not able to describe the phenomenon in its totality, and does not seem to permit an accurate modelisation of solid-plastic transitions. K. Kretzchmar [2] observed a similar behaviour at the time of an epoxy resin study, in which it was established that the kinetic homogeneous law, applied to Ellerstein's method, expresses only 40% of the phenomenon studied. Numerous authors [3–7] agree in thinking that it is often indispensable to compare results obtained in differential scanning analysis with results obtained in a different way to be able to decide between several reaction mechanisms. Thus, many [3–6] assert that it is necessary to carry out measurements by an isothermal method, to avoid some mistakes which could be committed during a kinetic study obtained only an-isothermally. Yang and Lee [7] propose comparison between a kinetic study obtained only an-isothermally. Yang and Lee [7] propose a comparison between a kinetic analysis obtained for DSC and one for FTIR, which appears to be more specific for studying the formation of some particular bonds.

Anisothermal kinetic program (KIN)

The program contains thirteen methods of kinetic treatment for differential scanning calorimetry (DSC) data.

Ozawa's method (1970) [8]

Considering the integral form of anisothermal kinetic equation:

$$g(\alpha) = \frac{k_o E_a}{RV} p(x) \tag{1}$$

Ozawa, using Doyle's approximation [9]:

$$\log p(x) = -2.315 - 0.4567\, x \tag{2}$$

obtains the equation:

$$\log V = -2.315 - 0.4567 \frac{E_a}{RT_p} - \log g(\alpha_p) + \log \frac{k_o E_a}{R} \tag{3}$$

Kissinger's method (1957) [10]

Kissinger uses the following approximation for $p(x)$:

$$p(x) = \frac{e^{-x}}{x^2} \tag{4}$$

$$g(\alpha_p) = \frac{k_o R T_p^2}{V E_a} e^{-E_a/RT_p} \tag{5}$$

$$\log(v/T_p^2) = -\frac{E_a}{R}\left(\frac{1}{T_p}\right) + \log\left(\frac{k_o R}{E_a}\right) - \log g(\alpha_p) \tag{6}$$

Kissinger's method imply that the maximum of the scanning rate suits the maximum of the DSC peak [11]. These two methods can be applied only if $g(\alpha_p)$ is a constant, i.e. if α_p is a constant for different scanning rates. In Eqs (3) and (6), one notes the presence of expressions $\log(k_o E_a/R)$ and $\log(k_o R/E_a)$ respectively, which implied that the transformation to be studied is governed by only one mechanism. This necessitates a restriction in the application of these methods, which, although they do not require knowledge of the reaction mechanism, therefore both imply that this last is the same for the whole process and is not dependent on the scanning rate. The computations showed [12] that we can estimate that the error is lower than 2% with Kissinger's method, and lower than 0.4% with Ozawa's. For each thermogram treated, the KIN program gives the peak temperature (T_p) and also that of α_p, to ensure that the model can be used.

Heat evolution methods

Differential methods

The differential methods are supported by the expression:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \cdot \Phi(\alpha, T) \tag{7}$$

There are still doubts about the possibility of separating this expression into two terms, the first solely dependent on the temperature, and the second on the transformed fraction, in the expression of the rate of reaction of materials in the solid state. In order to obtain the kinetic equation of the process, the function $\Phi(\alpha, T)$ is assumed to be equal to unity, so that the reaction rate is a unique function of conversion [13]:

$$\frac{d\alpha}{dt} = k\,(T)\cdot f\,(\alpha) \tag{8}$$

The temperature dependence of the formal rate constant is assumed to obey an Arrhenius-type law:

$$k(T) = k_o\cdot T^m\cdot e^{-E_a/RT} \tag{9}$$

Although the program permits computations for different m values with the ABS method (see below), the exponent m is generally assumed to be zero so that:

$$k(T) = k_o\cdot e^{-E_a/RT} \tag{10}$$

Malek's method (1989) [14]

This method requires the previous determination of activation energy, obtained by Kissinger's method. From E_a value, we can plot a standardized curve: $y(\alpha)$, whose aspect will depend on the mechanism involved. Thus, even if it seems impossible to find a general kinetic model for all processes occurring in the solid state [14], the method proposed by Malek permits a choice, among the three most used models, of the one we must retain, depending on the $y(\alpha)$ function's shape and on the value of α_p. The three models quoted are:

Reaction order (RO) model [15]

$$f\,(\alpha) = (1-\alpha)^n \tag{11}$$

where *n* is obtained according to Gorbatchev [16] by iteration of the equation:

$$\alpha_p = 1 - \left[\frac{2nRT_p + E_a}{nE_a + 2nRT_p}\right]^{1/n-1} \tag{12}$$

Johnson-Mehl-Avrami (JMA) model [17–18]

$$f\,(\alpha) = n\,(1-\alpha)\,[-\log\,(1-\alpha)]^{1-1/n} \tag{13}$$

where *n* is calculated from the maximal abscissa (α_M) of the normalized function $y(\alpha)$.

$$n = \left[\frac{1}{1+\log\,(1-\alpha_M)}\right] \tag{14}$$

Šestak-Berggren (SB) [19]

$$f(\alpha) = \alpha^m (1 - \alpha)^n \tag{15}$$

which Šestak, Šatava and Wendlandt [21] showed to be

$$\cong (1 - \alpha) [- \log (1 - \alpha)]^p \quad \text{with} \quad p = m / n \tag{16}$$

and

$$p = \alpha_M / (1 - \alpha_M), \quad n \text{ being the slope of the plot of}$$

$$\log \left[\frac{dH}{dt} \exp (E_a/RT) \right] vs. \log [\alpha^p (1 - \alpha)] \tag{17}$$

We can determine $\log k_0$ introducing $f(\alpha)$'s expression for each model [14]. The program offers the possibility of introducing the activation energy value, determined from several isothermal treatments at different temperatures (see further), and so, as with the Kissinger's method, without knowing the reaction mechanism. After calculating the kinetic parameter, by means of the appropriate model, it is possible to compute the activation energy relating to this model by plotting the corresponding Arrhenius straight line, and afterwards to recompute those parameters in the shape of an iterative calculation stopped when the desired convergence criterion is obtained.

$$\text{Convergence} = [E_a(i) - E_a(i - 1)] / E_a(i) \tag{18}$$

This way of proceeding, not present in the initial method of Malek, gives a much more precise modelisation of the calculated curve.

The following BD, SB, JMA (see below) differential methods are supported by the usually admitted kinetic law:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \tag{8}$$

$$\alpha = \frac{H}{Q_t} \text{ for DSC and } \alpha = \frac{w_i - w}{w_i - w_f} \text{ for TG data so:} \tag{19}$$

$$\frac{dH}{dt} \frac{1}{Q_t} = k_0 e^{-E_a/RT} f(\alpha) \tag{20}$$

for DSC data:

$$\log \left[\frac{dH}{dt} \frac{1}{Q_t} \right] - \log f(\alpha) = \log k_0 - \frac{E_a}{RT} \tag{21}$$

Borchardt-Daniel's (BD) method (1957) [20]

Where $f(\alpha) = (1-\alpha)^n$ is introduced in the Eq. (21), the reaction order is chosen which provides the best correlation coefficient for the Arrhenius plot.

Šestak-Berggren's (SB) method (1971) [19]

Where

$$f(\alpha) = \alpha^m(1-\alpha)^n[-\log(1-\alpha)]^p \tag{22}$$

For each parameter incremented the computation program tries all other values before going up to the superior increment. This can require considerable computation times. Meanwhile, in most cases, as shown by Šeštak [21], an iteration on m and n only is enough.

Johnson-Mehl-Avrami's method (1939) [17–18, 21]

Where $f(\alpha) = n(1-\alpha)[-\log(1-\alpha)]^{1-1/n}$, in which an iteration is executed on n (13).

The last three methods which return to the equation of models used in Malek's method, will permit comparisons between results obtained through two different approaches.

Achar, Brindley and Sharp's (ABS) method (1966) [12, 22]

For which we can choose among eight different terms for $f(\alpha)$:

A	:	$f(\alpha) = (1-\alpha)^n$	(11)
B	:	$f(\alpha) = n(1-\alpha)[-\log(1-\alpha)]^{1-1/n}$	(13)
C	:	$f(\alpha) = \alpha^n$	(23)
D	:	$f(\alpha) = \alpha^{-1}$	(24)
E	:	$f(\alpha) = [-\log(1-\alpha)]^{-1}$	(25)
F	:	$f(\alpha) = 3/2[(1-\alpha)^{1/3}-1]^{-1}$	(26)
G	:	$f(\alpha) = 3[(1-\alpha)^{2/3}]/[2(1-(1-\alpha)^{1/3})]$	(27)
H	:	$f(\alpha) = \exp(1-\alpha)$	(28)

we can retrieve in *A* and *B*, Borchardt-Daniels and Johnson-Mehl-Avrami's methods. The number of $f(\alpha)$ functions can be easily extended according to needs. The interest of this method lies in the numerous functions we can employ.

Freeman-Carroll's (FC) method (1958) [23]

The method has been modified in regard to the commercial software. It relies on the Arrhenius plot of the Eq. (29) which permits determination of E_a and n:

$$\frac{\log (dH / dt)_{i+1} - \log (dH / dt)_i}{\log (\Delta H_{i+1}) - \log (\Delta H_i)} = n - \left(\frac{E_a}{R}\right)\frac{(T_i - T_{i+1})}{[\log (\Delta H_{i+1}) - \log (\Delta H_i)](T_i \cdot T_{i+1})} \quad (29)$$

Log k_o is determined from the Eq. (21) for which $f(\alpha)=f(1-\alpha)^n$. The method available in the commercial software operates on a very different way:

– First, it is limited to the case where $n = 1$.
– It consists of seeking manually the interval of α for which n will be equal to unity. n is computed in the shape of differences between following points, while E_a and log k_o values are obtained from the preceding Eq. (21). It is, in fact, a matter of a BD method for which we state $n=1$. On the other hand, this way of proceeding unavoidably leads to some errors, which were brought to light at the time of the comparison between the calculated and the experimental curves with the aim of the Least Squares Method (LSM). Although the correlation coefficients obtained are often very good, in the commercial program these last relate to the calculation of E_a from Eq. (21) which is not the equation of a difference-differential method. The KIN program gives the correlation coefficient relating to the calculation effected in Eq. (29), called R, at the same time as that corresponding to Eq. (21), called RR for comparison. These equations have been employed to determine the kinetic parameters E_a and n from thermogravimetric curves with success, not only for the degradation of polymers, but also for simple inorganic decomposition reactions. However, at the same time they have been subjected to much criticism [21, 24–25]. Considering an approximately constant experimental scatter, the determination both at low and high conversions will be quite erroneous. Flynn and Wall [26] pointed out that the difference-differential method gives only a procedural n and E_a, particularly where an additional competitive or independent reaction takes place, and treatment of each linear-like range independently does little to improve results.

Ellerstein's method (1968) [27]

This method relies on the equation:

$$T_i^2 \frac{(d^2H / dT^2)_i}{(dH / dT)_i} = \frac{E_a}{R} - n \frac{T_i^2 (dH / dT)_i}{(\Delta H_i)} \quad (30)$$

We can note that for this method, the slope of the Arrhenius straight will give n, so we will here obtain a more accurate value for n than for that of E_a.

Compound mechanisms

There is a possibility presented by the software in view of differentiating several intervals from Arrhenius straight lines, and afterwards, determining kinetic parameters in the chosen intervals, with the help of the suitable $f(\alpha)$ model. The thermoanalytical curve is then plotted again; it is composed of the same number of parts as of the selected intervals. The computation of the standard deviation through the Least Squares Method (LSM) is realised relatively to each recalculated curve part, or globally.

Integral methods [12, 21]

In these methods, the difficulty consists of determining $g(\alpha)$, using a linear temperature programmation.

$$g(\alpha) = \int_{o}^{\alpha} \frac{d\alpha}{f(\alpha)} \tag{31}$$

$$g(\alpha) = \int_{T_o}^{T} k_o\, e^{-E_a/RT} \cdot \frac{dT}{V} \tag{32}$$

$$g(\alpha) = \frac{k_o}{V} \int_{T_o}^{T} e^{-E_a/RT} \cdot dT \tag{33}$$

Considering the term $\int_{o}^{T_o} e^{-E_a/RT} \cdot dT$ as negligible, the preceding integral (Eq. 33) becomes:

$$g(\alpha) = -\frac{k_o E_a}{RV} \int_{\infty}^{x} \frac{e^{-x}}{x^2} dx \tag{34}$$

$$g(\alpha) = \frac{k_o E_a}{RV} \int_{x}^{\infty} \frac{e^{-x}}{x^2} \cdot dx \tag{35}$$

$$g(\alpha) = \frac{k_o E_a}{RV} \cdot p(x) \tag{1}$$

Although Eq. (1) cannot be expressed in a closed form, there exist several series for its approximation [21]:

(1) For $x > 15$, according to Schlömilch

$$p(x) = \frac{\exp(-x)}{x(x+1)} \left[1 - \frac{1}{x+2} + \frac{1}{(x+2(x+3))} \cdots + \frac{(-1)^n A_n}{(x+2)...(x+n)}\right] \quad (36)$$

where A_n is a specific constant.

(2) For $9 < x < 174$:

$$p(x) = \frac{\exp(-x)}{x} \left(\frac{674.567 + 57.412x - 6.055x^2 - x^3}{1699.066 + 841.655x + 49.313x^2 - 8.02x^3 - x^4}\right) \quad (37)$$

(3) Or, for $20 < x < 60$, according to Doyle, the value for $\log p(x)$, given by Eq. (2).

Coats-Redfern's method (CR) (1964) [28]

This method uses the expression (38) for the integral of the second member:

$$\frac{RT^2}{E_a}(1 - \frac{2RT}{E_a}) e^{-E_a/RT} \text{ that gives :} \quad (38)$$

$$\log\left[\frac{g(\alpha)}{T^2}\right] = \log\left[\frac{k_0}{V}\frac{R}{E_a}(1 - \frac{2RT}{E_a})\right] - \frac{E_a}{RT} \quad (39)$$

Although this method is present in the software by right of comparisons, it is to be used cautiously, because it implies that the first term of the second member of Eq. (39) (containing T) is considered as constant, whence necessity to work on a reduced temperature interval. Some authors [21] specify that a plot of $\log\left[\frac{g(\alpha)}{T^2}\right]$ vs. $(1/T)$ should only give a straight line for α not exceeding 0.1.

Šatava's method (1971) [29]

Using Doyle's approximation [9], Šatava obtained the following equation:

$$\log g(\alpha) = -0.4567(\frac{E_a}{RT}) - 2.315 + \log(\frac{k_0 E_a}{RV}) \quad (40)$$

we can note that Eq. (40), like the preceding Eq. (39), implies that E_a is constant in the interval studied.

Zsakó's method (1968) [30]

The logarithmic form of Eq. (1) gives:

$$\log \frac{k_o E_a}{RV} = \log g\,(\alpha) - \log p(x) = B \tag{41}$$

where B depends only upon the nature of the compound studied and upon the scanning rate, but not upon temperature. The constancy of the difference $\log g\,(\alpha) - \log p(x)$ enables suggestion of a quantitative method of testing the validity of different kinetic equations of the same type and of determining the activation energy that can be estimated by finding the E_a value which ensure the maximum constancy of B. On the other hand, Zsakó [31] suggested that $\log p(x)$ may, to the first approximation, be a linear function of reciprocal absolute temperature. Mac Callum and Tanner [32] and Šatava [29] assumed further that, if the difference between functions of $\log g\,(\alpha)$ and $\log p(x)$ does not depend upon temperature, and if $\log p(x)$ is a linear function of $1/T$, then $\log g\,(\alpha)$ must also be a linear function of $1/T$. A plot of $\log g\,(\alpha)$ vs. $(1/T)$ computed from the experimentally obtained data, α and T, becomes linear for such a $g\,(\alpha)$ function which corresponds to the most probable rate-controlling process. This is true, as shown by Šeštak [33], for a temperature interval of process duration not exceeding 100°C. However, in the KIN program, Zsakó's method is not used to determine kinetic parameters (which can be obtained through another integral method, such Šatava's) but offers the possibility of selecting the proper reaction order and the proper mechanism in regard to the constancy of B. It is possible to choose between two types of approximation for $p(x)$:

$$p\,(x) = \frac{e^x}{(x+2)\,(x-d)} \quad \text{with} \quad d = \frac{16}{x^2 - 4x + 84} \tag{42}$$

or the $p(x)$ approximation given by Eq. (37). Bearing in mind the approximations the integrals methods proceed from.

Bearing in mind approximations the integrals methods proceed from.

They offer much more interest when we directly treat with α and t or α and T couples as in isothermal mode or in thermogravimetry.

Problems linked with the choice of the scanning rate

Low heating rates

These generally allow the obtaining of a better base line, at the same time as a better measure of temperatures; meanwhile they widen and flatten the DSC peaks [12]. On the other hand, considering the opposite processes as obeying the same rate-controlling process, we must consider [21]:

$$\frac{d\alpha}{dt} = k_{\text{for}} \cdot f(\alpha) - k_{\text{rev}} \cdot f(\alpha) = k_{\text{for}} \cdot f(\alpha)\left[1 - \exp\left(\frac{\Delta G}{RT}\right)\right] \tag{43}$$

Thus, the proper choice of a sufficiently high heating rate is essential for kinetic data computations, because at low heating rates the process is completed in the vicinity of the equilibrium temperature. Kinetic data calculated under such conditions are erroneous and E_a value is larger.

High heating rates

These give a better profile of DSC peaks, but create a removal effect of temperatures towards higher values, and reduce the base line stability. It should be remembered that in this manner some peaks can be hidden [12].

Choice of the mechanism selection criterion

There is a disagreement among authors with regard to the choice of this standard. Some of them [28–39] propose to retain the correlation coefficient as the criterion selection of reaction mechanism, others to compare the ratio of the standard deviations of the regression coefficient to its actual value [36]. Criado and Morales [6] have evoked the problem·of the relative significance we can accord to the correlation coefficient, depending on the number of points treated, and this could transmit some mistakes in interpretation.

One finds from the literature [36–40] that the correlation coefficient is not a good index for selecting the proper mechanism, and we must keep in mind that application of statistical criteria is only possible with the assumption that data have a 'normal distribution'. Since the aim of the calculations is to determine parameters that describe experimental data relatively well, the conformity of Yexperimental and Ycomputed (or α_{exp} and α_{calc}) is often used as a criterion for selecting the proper $f(\alpha)$ or $g(\alpha)$ function [5, 42, 43]. The standard kinetic evaluation method is the Least Squares Method [14].

Rozycki [5] proposed the calculation of R:

$$R = \frac{1}{n} \sum_{i=1}^{n} (\alpha_{calc,i} - \alpha_{exp,i})^2 \qquad (44)$$

where n is the number of experimental α values, $\alpha_{exp,i}$ the degree of conversion for a given temperature and $\alpha_{calc,i}$ the α value calculated.

The function with the minimum R value is selected as the one that best describes the experimental data. In our case the parameter calculated (called LSM) is obtained as mentioned by Rozycki [5] and used in addition to the correlation coefficient. The program presents the possibility of computing the kinetic parameters and/or treating several reaction mechanism, in an independent way, consisting in an isothermal treatment using again equations established in KIN, whose description follows.

Isothermal kinetic program KINISO

Series couple treatment (α, t)

Integral methods

Isothermally we have the Eq. (31) previously established [12]:

$$g(\alpha) = k(T) \cdot \int_0^t dt \qquad (45)$$

$$g(\alpha) = k_0 \cdot e^{-E_a/RT} \cdot t \qquad (46)$$

$$\log g(\alpha) - \log t = \log k_0 - \frac{E_a}{RT_{iso}} \qquad (47)$$

If we consider a time interval t, for which E_a is a constant (only one reaction mechanism), $\log g(\alpha) - \log t$ will also be a constant for a given temperature T_{iso}. The program computes $\log g(\alpha) - \log t = B$ for each couple, (α, t) then appreciates the variancy:

$$VAR = [(\sum B^2 - n B^2)/n]^{1/2} \qquad (48)$$

For a given mechanism, the reaction order selected is the one giving the lowest VAR value. Afterwards, we keep the mechanism giving the VAR minimal value. The different functions $g(\alpha)$ used are the same as the ones used in the integrals methods of KIN:

A	:	$g(\alpha) = 1-(1-\alpha)^n$	(49)
a	:	$g(\alpha) = (1-\alpha)^{-1}$	(50)
B	:	$g(\alpha) = [-\log(1-\alpha)]^{1/n}$	(51)
C	:	$g(\alpha) = \alpha^n$	(52)
D	:	$g(\alpha) = \alpha^2$	(53)
E	:	$g(\alpha) = (1-\alpha)[\log(1-\alpha)] + \alpha$	(54)
F	:	$g(\alpha) = (1-2/3\alpha) - (1-\alpha)^{2/3}$	(55)
G	:	$g(\alpha) = [1-(1-\alpha)^{1/3}]^{1/2}$	(56)
H	:	$g(\alpha) = \exp[-(1-\alpha)]$	(57)

Differential methods

From the Eq. (8) we obtain, for an isothermal temperature T_{iso}:

$$\log\left(\frac{d\alpha}{dt}\right) - \log f(\alpha) = \log k_o - \frac{E_a}{RT_{iso}} \qquad (58)$$

The way of proceeding is the same as that described previously for integral methods. The functions $f(\alpha)$ used suit the ones we find in Achar-Brindley-Sharp's (ABS) method.

E_a calculation in an isothermal way

From the Eq. (47) previously set, we note the t_c times for which we have a progress of reaction α_c (always chosen identical), so we will have $g(\alpha_c)$=constant.

$$\log t_c = \log g(\alpha_c) - \log k_o + \frac{E_a}{RT_{iso}} \qquad (59)$$

Log $g(\alpha_c)$–log k_o will be a constant for each isothermal measurement at a determined α_c. A plot of log t_c *vs.* $1/T_{iso}$ will give the E_a value [12]. It is essential to note that this does not require knowledge of the reaction mechanism to determine E_a (only to determine log k_o). The realisation of an isothermal measurement is supported by the hypothesis that the transformation of the material, during the time necessary to obtain the constant temperature, is negligible.

Kinetic program for thermogravimetric measurements: TGA

The TGA program will not be described here, previous kinetic equations of KIN, can be used in other studies, in order to add further results to those of the two previous techniques. Recent attempts were concerned with the goal of interpreting the complex reaction via parallel TG and DSC results [44–45]. Agrawal [45] has discussed some results of DSC and TG analysis, especially for the situation where different kinetic parameters can be obtained, stipulating if a reaction occurs with a change both in weight and in the heat of reaction, the kinetic parameters derived from TG and DSC under the same experimental conditions should be identical. The compounds studied in our laboratory showing an important vapor pressure, a thermogravimetric study could be considered as for the pentaerythritol [46], in view of establishing the temperature and the kinetics of sublimation of these compounds.

Conclusions

This kinetic software, elaborated from a wide bibliography and additional information, allows the study of a great number of physico-chemical processes.

This makes possible a comparison between results obtained through different techniques. For each data-recording technique, it is possible to choose amongst several kinetic processing methods, in order to obtain the best phenomenon characterization. For each method, several functions can be chosen, according to the reaction mechanism involved. Different approaches to this problem are possible with the help of different methods of procedure. This allows some cross-checkings between the results obtained to be established. Finally, the availability limits of each method are turned out in regard to the assumptions first stated, at the same time as some introduced approximations and some remarks concerning numerous authors' experiments. The experimental results obtained during this study will constitute the subject of a particular part, in which we will treat and develop their particularities and their important significations. The purpose will be to extend this software with the aim of being able to treat any recording of the temperature variation dependent on the time, and establishing comparisons between the results provided from different techniques.

List of symbols

E_a	:	activation energy	($kJ \cdot mol^{-1}$)
$k(T)$	:	specific rate constant	(s^{-1})
k_o	:	pre-exponential factor	(s^{-1})
R	:	universal gas constant	($8.314\ kJ \cdot mol^{-1} \cdot K^{-1}$
V	:	scanning rate	$(K \cdot s^{-1})$
T	:	absolute temperature	(K)
T_p	:	top of peak temperature	(K)
α	:	degree of conversion	
α_p	:	degree of conversion to the top of the peak	
α_M	:	degree of conversion corresponding to the maximum of the peak function $y(\alpha)$	
m, n, p	:	kinetic exponents	
$y(\alpha)$	:	standardized curve	(see [14])
$d\alpha/dt$	:	reaction rate	(s^{-1})
dH/dt	:	heat flow (and also Y)	(mW)
H_i	:	partial enthalpy at the temperature T_i	(J/g)
Q_t	:	total enthalpy	(J/g)
ΔH_i	:	$Q_t - H_i$	(J/g)

k_{for}	:	constant rate of the forward reaction	(s^{-1})
k_{rev}	:	constant rate of the reverse reaction	(s^{-1})
ΔG	:	Gibbs free energy	(J/g)
t	:	time	(s)
T_{iso}	:	isothermal temperature	(K)
x	:	E_a/RT	
w	:	weight loss	(mg)
w_i	:	initial weight	(mg)
w_f	:	final weight	(mg)

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Zusammenfassung — Cu(II)-komplexe von Acenaphthoquinonmono-(4-methyl-quinolinyl)-hydrazon (AMH) der allgemeinen Zusammensetzung [CuLX$_2$] (mit L = AMH; X = Cl, Br, I, OAc oder NO$_3$) -ausgenommen die Sulfato-komplexe, die über die allgemeine Zusammensetzung [CuLSO$_4$]$_2$ verfügen – wurden hergestellt und mittels Elementaranalyse, Messungen des magnetischen Momentes, Leitfähigkeitsmessungen, IR, elektronen- und EPR-spektroskopischen Techniken und durch Thermoanalyse untersucht. Für alle Komplexe wurde eine planare Geometrie gefunden. Die TG-Kurven zeigen, daß die Komplexe in einem Schritt zersetzt werden, wobei am Ende dieses Schrittes Cu$_2$O gebildet wird.