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ANALYSIS OF THE THERMOKINETICS UNDER DYNAMIC CONDITIONS BY RELATIVE RATE OF THERMAL DECOMPOSITION

A. Mianowski

Silesian Technical University, Department of Chemical Technology of Coal and Petroleum,
Krzywoustego 8, 44-100 Gliwice, Poland

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Abstract

A novel parameter of the relative rate of thermal decomposition has been defined on the basis of an analysis of equation relating the logarithm of the conversion degree on the temperature. The dependence of this parameter on temperature in the dynamic conditions has been analyzed and discussed. The dependence of the relative rate of thermal decomposition is a linear relationship involving two coefficients. These coefficients can be related to the enthalpy and activation energy. The parameter developed has been used for the analysis of a series of consecutive reactions of thermal decomposition of calcium oxalate monohydrate.

Keywords: calcium oxalate monohydrate, conversion degree, relative rate, thermal decomposition, thermokinetics

Introduction

It is very common under dynamic conditions that using a conversion degree of the substrate the rate of thermal decomposition of a solid can be given by the equation in which a rate constant fulfils the classical Arrhenius equation [1–3].

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A}{q}\mathrm{e}^{-\mathrm{E/RT}}f(\alpha),\quad q>0,\ 0\leq\alpha\leq1 \tag{1}$$

The relationship between time and temperature is most often described by a linear equation:

$$T=T_\mathrm{i}+q\tau \tag{2}$$

Therefore starting from the total differential:

$$\mathrm{d}\alpha=\left(\frac{\partial\alpha}{\partial\tau}\right)_\mathrm{T}\mathrm{d}\tau+\left(\frac{\partial\alpha}{\partial T}\right)_\tau\mathrm{d}T \tag{3}$$

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we obtain the following formula:

$$\mathrm{d}\alpha = A\mathrm{e}^{-\mathrm{E/RT}} f(\alpha)\left[\mathrm{d}\tau + \frac{E\tau}{RT^2}\mathrm{d}T\right] \tag{4}$$

After substituting relationship (2) into Eq. (4) twice, i.e., $\mathrm{d}T/\mathrm{d}\tau = q$ and $\tau = T/q$ ($T_i = 0$ K [4, 5]) we finally obtain a formula:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{q}\,\mathrm{e}^{-\mathrm{E/RT}} f(\alpha)\left[1 + \frac{E}{RT}\right] \tag{5}$$

We can also obtain a similar equation for the reaction rate in a form of [6]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{q}\mathrm{e}^{-\mathrm{E/RT}} f(\alpha)\left[1 + \frac{2RT}{E}\right] \tag{6}$$

Equations (5) and (6) are too complex to be used, therefore, the most simple form given by Eq. (1) continues to be widely applied.

The aim of the work

The relationship developed in previous publications [7] is the starting point for this analysis:

$$\ln\alpha = a_0 - \frac{a_1}{T} - a_2\ln T, \quad 0 < \alpha \le 1 \tag{7}$$

This formula is to be used to estimate the relative rate of thermal decomposition as a function of temperature.

Analysis of the basic relationship (7)

Relative rate of thermal decomposition

Let us analyse relationship (7) in which the coefficients take only the signs given in the equation. The signs of the a_0, a_1 and a_2 coefficients can also admit reverse signs, it was discussed in previous publications [7], but we here omitted such a possibility in the current discussion.

The differentiation of Eq. (7) results in:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \alpha\left(\frac{a_1}{T^2} - \frac{a_2}{T}\right) \tag{8}$$

which can be rearranged to the more convenient:

$$r = \frac{\mathrm{d}\alpha/\mathrm{d}T}{\alpha}T^2 = -\frac{\mathrm{d}\ln\alpha}{\mathrm{d}(1/T)} = a_1 - a_2 T \tag{9}$$

Relationship (9) is linear and a dimension of the relative rate r is degree Kelvin.

The term of $[(d\alpha/dT)/\alpha]T^2$ or $[-d\ln\alpha/d(1/T)]$ which appeared in Eq. (9) could be expressed differently, employing the quantities used by thermal analysis T, TG and DTG that results in the fact that we do not need to know the final mass of the sample that would otherwise be necessary for the calculation of the conversion degree (we omit here the proof) [8]:

$$r_{\mathrm{TG}} = -\frac{DTG}{m_{\mathrm{i}} - TG}\left(\frac{T}{100}\right)^2 \tag{10}$$

The practical use of Eq. (9) should take into account both mathematical formalism and results of experimental observations for the boundary values of $\alpha=0$ and $\alpha=1$, or just in the neighbourhood of these values:

1. relationship (7) gives inequality:

$$a_0 - a_1/T < a_2 \ln T \tag{11}$$

which arises from the condition $\alpha<1$.

For the equality sign in relation (11) the condition of $\alpha=1$ is fulfilled.

2. For the condition of $d\alpha/dT=0$ we obtain from Eq. (8):

$$\left.\begin{array}{l} T^* = \dfrac{a_1}{a_2}, \quad a_2 \neq 0 \\ \text{or} \quad \alpha = 0 \end{array}\right\} \tag{12}$$

and finally

$$r = a_2(T^* - T) \tag{13}$$

T^* is the temperature for which the function resulting from the transformation of (7):

$$\alpha = \frac{\exp\left(a_0 - \dfrac{a_1}{T}\right)}{T^{a_2}} \tag{14}$$

assumes the maximal value.

T^* often describes unrealistic case (Fig. 1) since in reality α cannot exceed unity (Eq. (1)). This maximum can arouse in a range of $\alpha>1$, but one can also take into account that maximum value can appear just in the nearest neighbourhood of $\alpha=1$. Such a case needs special analysis and it cannot be excluded that relationship (7) should be narrowed to a certain conversion degree.

3. The rate of decomposition $d\alpha/dT=0$ for α=idem. Such a case appears for $\alpha=0$ and $\alpha=1$. Although for $\alpha=0$ Eq. (1) generates the decomposition rate of a certain value, practical experiments show that near the boundary values, $d\alpha/dT$ amounts to 0 or is negligibly low (Fig. 2). This means that sometimes we should resign from the experimental points within these ranges or a few points of the very low rate for the initial and/or final stages of the reaction should be omitted during the normalization

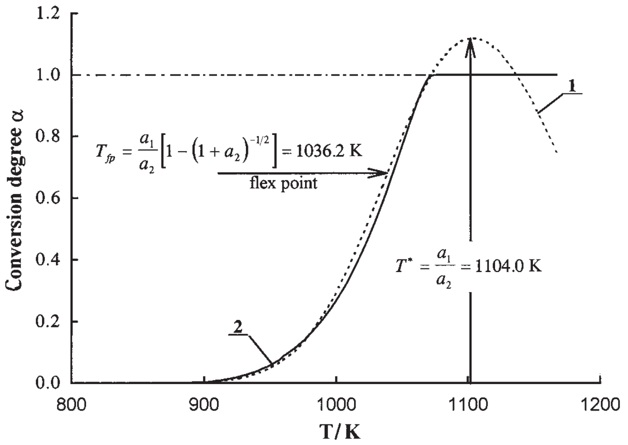

Fig. 1 The dependence of degree of conversion on the temperature of $CaCO_3$ resulting from the thermal decomposition of $CaC_2O_4 \cdot H_2O$; 1 – Eq. (7), entry (III) in Table 1 for data of N=95; 2 – experimental data

of the TG profile to conversion degree. The analysis should be extended to include a condition $d^2\alpha/dT^2=0$. From Eq. (8) we obtain then flex point on the left:

$$T_{\mathrm{fp}} = \frac{a_1}{a_2}[1-(1+a_2)^{-1/2}] \tag{15}$$

which underlines the meaning of the value of the a_2 coefficient for this analysis (Fig. 1).

Physical and chemical meaning of the a_1 and a_2 coefficients

The analysis performed in [7] proves that the higher the value of a_2 is the larger the deviation from the equilibrium.

Starting from Eq. (13) a_2 can be brought into the form of:

$$a_2 = -\frac{\mathrm{d}r}{\mathrm{d}T} \tag{16}$$

After substitution the finite differences, using the Lagrange equation we obtain the following formula giving a mean value of:

$$a_2 = -\frac{r(T_{\mathrm{f}})-r(T_{\mathrm{i}})}{T_{\mathrm{f}}-T_{\mathrm{i}}} \tag{17}$$

As $r(T_{\mathrm{f}})=0$, $r(T_{\mathrm{i}})=r_{\mathrm{i}}$, then finally:

$$a_2=\frac{r_i}{\Delta T_r},\quad \Delta T_r=T_f-T_i\leq T^*-T_i \tag{18}$$

The dimensionless a_2 coefficient is proportional to an initial relative rate and inversely proportional to the temperature interval in which total decomposition of the analyzed compound takes place. Equation (18) explains, to some extent, the problems associated with the exact separation of equilibrium reactions ($a_2=0$) from the thermokinetic ones ($a_2>>>0$) for low values of a_2 of the order of 50 units. For $a_2=0$ Eq. (7) reduces to a modified van't Hoff equation, which is presented in references [5, 9–21], while Eq. (9) takes the form of:

$$\frac{d\alpha}{\alpha dT}T^2=a_1=\text{idem},\quad a_2=0 \tag{19}$$

The following formula operates for a conversion degree attaining equilibrium value, $\alpha=\dot{\alpha}$:

$$a_1=\frac{\Delta H}{\nu R} \tag{20}$$

It can be assumed that the a_1 and a_2 coefficients in Eqs (7)–(9), (13) and (14) are of thermokinetic and kinetic meaning, respectively, which however needs further commentary.

Thus, according to [7] identical mathematical structure is shown by:

1. temperature criterion (for low conversion degree) [22],
2. thermokinetic equations of the R1 (0-order kinetics) and/or D1 (diffusion model), which are the approximations of the temperature integral according to Doyle [23].

Moreover, it can be noted that during generation of thermokinetic profiles one can make use of the thermodynamic threshold, which is related to the enthalpy of thermal decomposition [24]. Even if we assume that $a_2=0$ it should be assumed more carefully that a_1 is of much more complicated nature than that given by Eq. (20). Eventually, the a_1 coefficient can be related to activation energy.

Experimental results

A Mettler TG-50 apparatus of the TA-400 thermoanalytical system was used to carry out the measurements. The TG and DTG profiles shown as functions of temperature in Fig. 2, give the temperature calculated according to Eq. (2) in degrees centigrade, obtained by a heating rate of $q=1/6$ K s^{-1} and initial weighted portion of $m_i=30.838$ mg. The analyses were performed under argon. The TG profile was registered at ΔT amounting to 1 K and data for a constant step of $\Delta T=3$ K were used for further calculations.

The current publication shows the results only for the calcium oxalate monohydrate which decomposes under experimental conditions in three steps [25]:

$$CaC_2O_4\cdot H_2O\rightarrow CaC_2O_4+H_2O_{(g)} \tag{I}$$

$$CaC_2O_4 \rightarrow CaCO_3 + CO_{(g)} \qquad \text{(II)}$$

$$CaCO_3 \rightarrow CaO + CO_{2(g)} \qquad \text{(III)}$$

The results of calculations are given in Table 1. Figures 3 and 4 are graphical illustrations of the results obtained. Straight line **1**, shown in Fig. 4, is plotted according to Eq. (9) for the coefficients of a_1 and a_2 given in Table 1 (the data – Fig. 3).

Points corresponding to **2** are obtained by calculation of the finite differences $\Delta\alpha/\Delta T$, while ascribing a decomposition rate of 0 to the latter temperature. The points

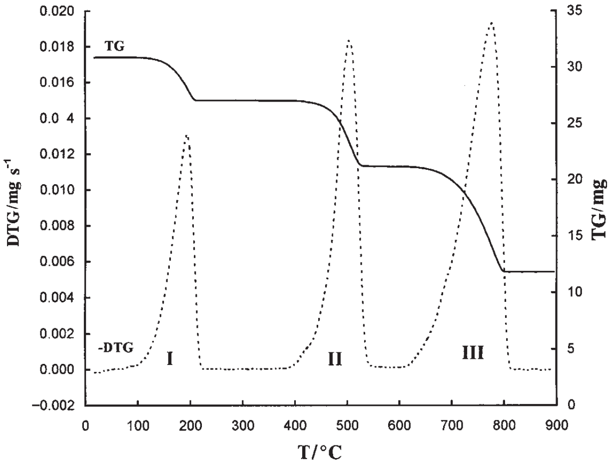

Fig. 2 The thermal decomposition of $CaC_2O_4 \cdot H_2O$, the TG and DTG profiles shown as the functions of temperature (exclusively in this Figure the dimension of DTG is mg s^{-1}, q=1/6 K s^{-1})

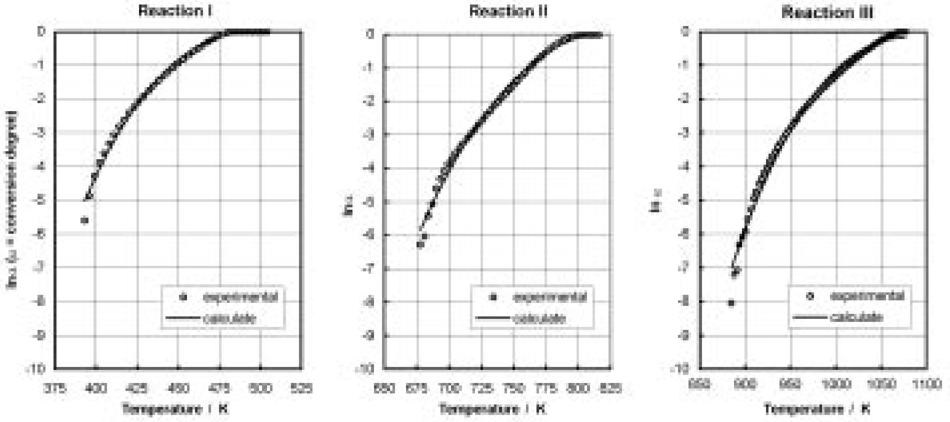

Fig. 3 An analysis of the relationship (6) for the three consecutive reactions of thermal decomposition of $CaC_2O_4 \cdot H_2O$, (I), (II) and (III) shown in semilog scales; – Eq. (7) entries system (I), (II) and (III) in Table 1 the superscipt of b; o – experimental data

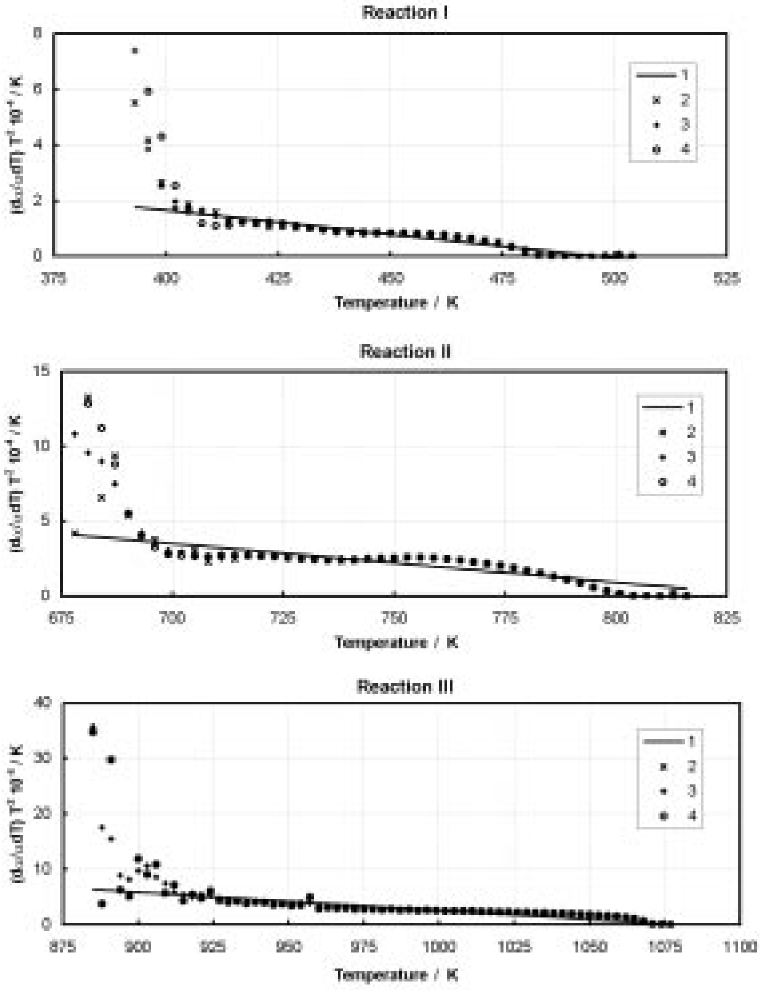

Fig. 4 An analysis of the relationship between the relative rate of thermal decomposition (9) and temperature for the three consecutive reactions of (I) (II) and (III); 1 – Eq. (9) for the coefficients of Eq. (7); 2 – experimental data $r=(\Delta\alpha/\Delta T)(T^2/\alpha)$; 3 – for conversion degree smoothed with a simple moving average procedure for three points; 4 – as above, but using a polynomial of the 8th or 9th order

expressed in **3** and **4** represent data smoothed by processing various conversion degrees only, because ΔT takes a constant value.

Points corresponding to **3** result from the smoothing of α by a procedure of so-called simple moving average performed for three points and points **4** with 8th or 9th order polynomials. The differentiation was performed after smoothing the data with Statgraphics 5.0 software program running on a PC.

Table 1 The estimation of the relationship (7) and calculations of the characteristic temperature describing the reactions of decomposition of $CaC_2O_4{\cdot}H_2O$ (I), (II) and (III). Significance level=0.0000

Reaction	Number of data	Range of α and temperature	Equation (7)			R^2/%	Test F	T^*/K Eq. (12)	T_{fp}/K Eq. (15)	$T_{max}{}^{a}$/K	$T_{0.99}{}^{d}$/K
			a_0	a_1	a_2						
(I)	38^b	$3.71{\cdot}10^{-3}$–0.9981 373–504 K	1240.56	$8.5369{\cdot}10^4$	172.15	99.29	2431.3	495.9	458.2	468	483
(II)	70	$1.87{\cdot}10^{-3}$–1 678–885 K	1927.77	$2.0876{\cdot}10^5$	249.39	99.27	4536.8	836.8	783.9	777	813
	47^b	$1.87{\cdot}10^{-3}$–0.9918 678–816 K	2003.06	$2.1630{\cdot}10^5$	259.22	99.24	2878.0	834.4	782.7		
(III)	95^c	$3.21{\cdot}10^{-4}$–1 885–1167 K	2114.43	$2.9153{\cdot}10^5$	264.07	98.96	4379.89	1104.0	1036.2	1050	1071
	65^b	$3.21{\cdot}10^{-4}$–0.9997 885–1077 K	2597.28	$3.5110{\cdot}10^5$	325.33	98.88	2745.81	1079.2	1019.5		

[a] Estimated experimentally; [b] Fig. 3; [c] Fig. 1; [d] Temperature for which α≈0.99

Discussion

Equation (14) describes the relationship between conversion degree and temperature for the three chemical reactions analyzed (I)–(III) as shown in Table 1. Further analysis presented in Fig. 3 indicates that the calculations should be performed, for several points neglecting if possible, points corresponding to very high and low conversion degree, of the order of $\alpha=0.001$ or $\alpha=0.99$. It is also advisable to use Eq. (12) to monitor a range within which a function (14) takes maximum value. From the methodological point of view the value of the temperature T^* should be higher than the temperature for which $\alpha\approx0.99$. The more accurate the approximation (e.g. estimated with the determination coefficient R^2) the more closely is the relation between the experimentally estimated temperature of the maximal reaction rate and the T_{fp} value that is obtained from Eq. (15). Moreover, Fig. 4, which illustrates the analysis of the dependence of the relative rate of thermal decomposition under dynamic conditions according to Eq. (9), clearly indicates high deviations of the reaction path from the temperature for the initial stages. The same effect can be observed for the final stage of the reaction, if one takes a linear relationship (9) as a criterion. The deviation for the initial stages can be explained by the error resulting from the numerical differentiation of the data, in particular, during the estimation of $[(\mathrm{d}\alpha/\mathrm{d}T)/\alpha]T^2$ for $\alpha\rightarrow0$ because in such a case $r\rightarrow\infty$. For the final stage, the situation is reversed, i.e. $r\rightarrow0$. The nature of these effects cannot be changed by the smoothing procedure of the data; in this particular case it is only the extent of the deviations from a straight-line plot that can be observed. The graphic profiles (Fig. 4) of the relationship within the medium range are also interesting, showing some deviations of plot Eq. (9) from linearity. Despite those effects the analysis shown in Fig. 4 can provide further valuable information explaining the complexity of undergoing processes.

Although the thermodynamic analysis of the reaction (I)÷(III) was not the main issue of the current publication, the examination of Figs (3) and (4) together with Table 1 results in several important conclusions of the thermodynamic nature.

As given below the individual values of the a_2 coefficient define the rank illustrating the distance from the decomposition in equilibrium conditions (the a_2 values are given in brackets):

$$\text{Equilibrium}<\text{I }(172.2)<\text{II}(249.4\text{–}259.2)<\text{III}(264.1\text{–}325.3) \tag{21}$$

It can be easily found that the same ranks will appear if the relative rate of decomposition according to Eq. (9) is used. In this particular case, the growing influence of the kinetics term explains this effect.

Finally, if we take after the reference [26] the theoretical standard decomposition enthalpy of: $\Delta H_{298}(\mathrm{I})=36.4$, $\Delta H_{298}(\mathrm{II})=85.4$, $\Delta H_{298}(\mathrm{III})=209.0$ kJ mol^{-1} and put together the Eqs (9), (19) and (20) for $\nu=1$, then we obtain the constant values of the relative rate of reaction in equilibrium, irrespective of temperature. Thus, for reaction (I) to (III) we obtain:

$$r(\mathrm{I})=0.44\cdot10^4\ \mathrm{K},\ r(\mathrm{II})=1.03\cdot10^4\ \mathrm{K},\ r(\mathrm{III})=2.51\cdot10^4\ \mathrm{K},\ \text{when } a_2=0. \tag{22}$$

The relative rates calculated are low and they are reached just before the completion of the decomposition.

Conclusions

1. The relationship (7) proposed, which relates the conversion degree of thermal decomposition to the temperature forms an interesting criterion enabling one to distinguish between equilibrium and thermokinetic reactions. Moreover, the relative rate of thermal decomposition given by Eq. (9) can be derived on the basis of this equation. Such a parameter depends linearly upon the temperature according to Eqs (9) and (13).

2. Further information for the interpretation of the process taking place can be gained by plotting the results as the function

$$r=\frac{\mathrm{d}\alpha/\mathrm{d}T}{\alpha}T^2=-\frac{\mathrm{d}(\ln\alpha)}{\mathrm{d}(1/T)}=-\frac{DTG}{m_\mathrm{i}-TG}T^2 \ \mathit{vs}.\ \text{temperature}$$

The dotted diagrams are characterized by the deviations from a linear plot (9) and (13) appearing for the initial and final stages; for the TG profile within the whole range analyzed. The lack of the dependence of r=idem upon temperature indicates the equilibrium progress of the reaction.

3. The coefficients of a_1 and a_2 have a clear physical meaning. They appear in equations describing characteristic temperatures T^* (12) and T_fp (15). The a_1 coefficient is proportional to the enthalpy of thermal decomposition, if the experimentally estimated conversion degree corresponds to the equilibrium one (Eq. (20)). On the other hand, the a_2 coefficient is closely related to the relative rate of thermal decomposition (Eq. (13)) and is proportional to the initial relative rate and inversely proportional to the temperature interval in which the total decomposition of the substance takes place. The meaning of these coefficients is, however, different. The a_2 coefficient reflects mainly kinetic nature, while a_1 (if $a_2 \neq 0$) dual thermodynamic and kinetic features.

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Symbols

a_0, a_2 – dimensionless coefficients in Eq. (7),
a_1 – coefficient in Eq. (7)/K,
A – frequency constant in Arrhenius equations/s^{-1},
E – activation energy/J mol^{-1}
F – F test,
$f(\alpha)$ – symbol of the mechanism/process,

ΔH – enthalpy/J mol^{-1}
m – mass, i.e., mass loss on heating curve TG/mg,
N – population of data,
r – relative rate of thermal decomposition of chemical compounds/K,
r_{TG} – relative rate as a complex quantity (T/K, TG/mg, DTG/mg K^{-1})/K,
$R = 8.314$ J mol^{-1} K^{-1}
R^2 – determination coefficient/%
q – heating rate/K s^{-1}
t, T – temperature/°C or K.

Greek symbols

α – conversion degree, $0\leq\alpha\leq1$,
$\dot{\alpha}$ – equilibrium conversion degree, $0\leq\dot{\alpha}\leq1$,
ν – stoichiometric coefficient, in this work: gaseous phase,
τ – time/s,
Δ – a finite difference.

Subscripts

i – initial,
f – final,
fp – flex point,
max – experimental maximal value,
r – refers to reaction.

Superscripts

* - a maximal point in formal meaning.

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