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# THREE-PARAMETRIC EQUATION IN EVALUATION OF THERMAL DISSOCIATION OF REFERENCE COMPOUND

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Further considerations concerning thermal decomposition of reference material – $CaCO_3$, described by three-parametric equation in version (3), have been presented. It was established that in linear relationship between coefficients of Eq. (3) $a_2$ is the argument of $a_1$, which reaches minimal value of thermodynamic character ($\Delta H/vR$) when $a_2=0$ (equilibrium relationship). During thermal decomposition connection between system atmosphere – rich in $CO_2$ or vacuum, caused by fast evacuation of gaseous products – and activation energy value, as well as maximal temperature of reaction process. Conditions of this kind may be explained by Zawadzki–Bretsznajder law.

***Keywords:*** *maximal rate of reaction/process, thermodynamics vs. kinetics, three-parametric equation, Zawadzki–Bretsznajder law*

## Introduction

Analysis of Holba–Šesták equation (H–S) [1–4] in [5] broadened authors assumptions in meaning that generalization in form of three-parametric equation was proved as a consequence of their considerations.

Starting from three-parametric form [6]:

$$\ln\alpha = a_0 - \frac{a_1}{T} - a_2 \ln T \tag{1}$$

for experimentally determined condition:

$$T = T_f, \text{ when } \alpha = 1 \tag{2}$$

one obtains two-parametric equation:

$$\ln\alpha = a_1\left(\frac{1}{T_f} - \frac{1}{T}\right) - a_2 \ln\frac{T}{T_f} \tag{3}$$

From Eqs (1) and (3) originates relative rate of reaction/process [7]:

$$r = \frac{d\alpha}{\alpha dT} T^2 \tag{4}$$

which is linear relationship:

$$r = a_1 - a_2 T \tag{5}$$

Positively, for $T=T_f$, $\alpha=1$, then $r=0$, because $d\alpha/dT=0$. Yet, according to Eq. (5), when $r=0$, then $T^* = a_1/a_2 (a_2 \neq 0)$, but predominantly $T_f < T^*$ [7].

The aim of the work is expanding knowledge of next elements of three-parametric Eq. (1) interpretation in version (3) for thermal decomposition of reference material, $CaCO_3$. The basis of considerations are results of investigations described and discussed in works [8–11], completed with analysis of simulated, as well as own and literature data.

## Analyzed data

1 Results of $CaCO_3$ thermal decomposition analyzed in [8–11] were obtained from Prof. M. E. Brown for two versions:

- decomposition in dynamic conditions for following heating rates: $q$=1, 3, 5, 7.5, 10, 15 and 25 K $min^{-1}$ (Fig. 2 in [8]),
- decomposition in dynamic conditions in vacuum for following heating rates: $q$=1.8, 2.5, 3.5, 5, 6.2 and 10 K $min^{-1}$ (Fig. 1 in [8]).

2 Results of $CaCO_3$ thermal decomposition simulation obtained as a result of assumed constants in a way similar to the one presented in [12] for differential equation:

$$\frac{d\alpha}{dT} = \frac{A}{q} e^{-\frac{E}{RT}} \left[1 - \left(\frac{\alpha}{\alpha_{eq}}\right)\right]^n \tag{6}$$

where for $T \leq T_{eq}$:

$$\ln\alpha_{eq} = \frac{\Delta H}{vR}\left(\frac{1}{T_{eq}} - \frac{1}{T}\right) \tag{7}$$

and for $T > T_{eq}$:

$$\alpha_{eq} = 1 \tag{8}$$

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Equation (6) was solved with the use of 4th order Runge–Kutta method for constants: $E$=220 kJ mol$^{-1}$, $\Delta H$=176 kJ mol$^{-1}$, $A$=34.7·10$^{6}$ min$^{-1}$, $q$=10 K min$^{-1}$, $T_{eq}$=1157.4 K, $n$=0, 1/2; 1 and 2.

3 Literature data of $CaCO_3$ thermal decomposition, what allowed determining coefficients of Eqs (1) or (3).

4 Results of $CaCO_3$ thermal decomposition in $CO_2$ atmosphere (number of data $N$=56), carried out using derivatograph Q-1500D in following conditions: Pt crucible, sample mass: 96 mg, reaction temperature range: 874–929°C, heating rate $q$=10 K min$^{-1}$, gas flow rate of $CO_2$: 2.5 cm$^3$ min$^{-1}$.

### *Results of investigations for reference material $CaCO_3$*

Decomposition in dynamic conditions, $p$=const.

Results of calculations are presented in Tables 1 and 2 presents:

- estimation of Eq. (3) coefficients: $a_1$ and $a_2$ for $a_0$=0, and experimentally determined temperature $T_f$ for $\alpha$=1,
- estimation of temperature $T^*=a_1/a_2$ according to Eq. (5) for $r$=0,
- experimentally determined temperature of maximal reaction rate $T_m$ and corresponding conversion degree $\alpha_m$,
- experimentally determined derivative d$\alpha$/d$T$ for $T$=$T_m$ and calculated according to formula [5] (Eqs. (I-5) in [5]):

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{T=T_m}=\frac{\alpha_m}{T_m}(1+\sqrt{1+a_2}) \qquad (9)$$

Equation (9) may be used in different ways, e.g. by individual calculation of $\alpha_m$ and $T_m$. The method often leads to unexpected results, because relation $T_m$>$T_f$ may be observed (compare comments to Eqs (I-7) and (I-8) in [5]). Therefore, the compensatory calculations were carried out by modulation of relationship $\alpha$ *vs.* $T$ with 6 degree polynomial. Then, smoothed data obtained this way were substituted into Eq. (6), in the next step using values of $a_2$ given in Table 1. From Fig. 1 follows that such method of results interpretation is necessary. The thesis, which should follow from Table 1, is to prove that the following inequality (mentioned also in [5], Eq. (23)) is valid for $\alpha_{eq}$=1 and in this case $v$=1:

$$\left(\frac{\mathrm{d}\alpha_{eq}}{\mathrm{d}T}\right)_{T=T_{eq}}\geq\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{T=T_m} \qquad (10)$$

$$\alpha_{eq}\frac{\Delta H}{vRT_{eq}^2}=\frac{\Delta H}{RT_{eq}^2}\geq\frac{\alpha_m}{T_m}(1+\sqrt{1+a_2}) \qquad (11)$$

From Table 1 follows that postulated inequality is valid. Experimental results show that maximal de-

**Table 1** The results of calculations for thermal dissociation of reference $CaCO_3$, $a_0$=0, significance level=0.0000

| q/ K min$^{-1}$ | $a_1$/ K | $a_2$ | $T_f$/ K | $\rho^2$ | $T^*=a_1/a_2$/ K | $\alpha_m$$^a$ | $T_m$$^a$/ K | (d$\alpha$/d$T$)$_{max}$$^a$/ K$^{-1}$ | (d$\alpha$/d$T$)$_{max}$ acc.(9)/ K$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 222790.0 | 207.64 | 999.20 | 0.9994 | 1072.96 | 0.88194 | 990.50 | 0.01914 | 0.01375 |
| 3 | 149120.3 | 126.70 | 1043.15 | 0.9998 | 1176.96 | 0.85085 | 1029.63 | 0.01724 | 0.01016 |
| 5 | 117022.3 | 92.66 | 1066.15 | 0.9999 | 1262.92 | 0.96864 | 1060.82 | 0.01741 | 0.00975 |
| 7.5 | 90869.3 | 65.73 | 1084.15 | 0.9996 | 1382.46 | 0.76296 | 1065.15 | 0.01664 | 0.00657 |
| 10 | 92399.4 | 66.22 | 1099.15 | 0.9998 | 1395.34 | 0.96746 | 1093.27 | 0.01562 | 0.00814 |
| 15 | 95042.6 | 67.57 | 1020.15 | 0.9998 | 1406.58 | 0.88495 | 1108.21 | 0.01607 | 0.00741 |
| 25 | 91803.4 | 63.00 | 1144.15 | 0.9997 | 1457.20 | 0.83630 | 1127.59 | 0.01487 | 0.00668 |

[a]experimenal value

**Table 2** The results of calculations for thermal dissociation of $CaCO_3$ in vacuum, $a_0$=0, significance level=0.0000

| q/ K min$^{-1}$ | $a_1$/K | $a_2$ | $T_f$/K | $\rho^2$ | $T^*=a_1/a_2$/ K | $\alpha_m$$^a$ | $T_m$$^a$/K | (d$\alpha$/d$T$)$_{max}$$^a$/ K$^{-1}$ | (d$\alpha$/d$T$)$_{max}$ acc.(9)/ K$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1.8 | 567864.2 | 660.62 | 867.15 | 0.9976 | 859.59 | 0.72539 | 834.81 | 0.01872 | 0.02322 |
| 2.5 | 506617.3 | 577.55 | 883.15 | 0.9981 | 877.18 | 0.54916 | 840.10 | 0.01684 | 0.01638 |
| 3.5 | 417727.5 | 465.52 | 904.15 | 0.9986 | 897.34 | 0.57794 | 856.55 | 0.01476 | 0.01525 |
| 5 | 391060.3 | 426.98 | 921.15 | 0.9987 | 915.87 | 0.74636 | 885.19 | 0.01398 | 0.01829 |
| 6.2 | 380538.5 | 410.49 | 933.15 | 0.9985 | 927.03 | 0.53396 | 878.97 | 0.01361 | 0.01293 |
| 10 | 304673.9 | 316.62 | 962.15 | 0.9983 | 962.27 | 0.73883 | 921.83 | 0.01233 | 0.01509 |

[a]experimental value

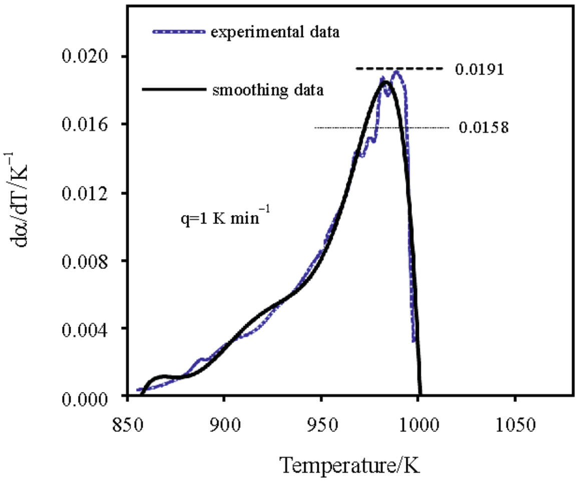

**Fig. 1** Relationship between the reaction rate (d$\alpha$/d$T$) and temperature ($T$) for thermal dissociation of reference $CaCO_3$ ($q$=1 K min$^{-1}$, Table 1 in [8])

composition rate is lower than the one following from relationship $\alpha_{eq}$ *vs.* $T$ in temperature $T_{eq}$. One may also observe that coefficient $a_2$ decreases together with heating rate from $a_2$=207.64 to ca. $a_2$=63–68. According to the previous work [7] the values are close to the criterion used for equilibrium relationships. In this case equilibrium line is determined by Eq. (7). It turns out that all curves $\alpha$ *vs.* $T$ are on the left side of the equilibrium curve, thus they do not satisfy relation $\alpha<\alpha_{eq}$. It means that coefficient $a_2$ is not so much a measure of deviation from equilibrium state as information about deformation of relationship $\alpha_{eq}$ *vs.* $T$. In other words, for large values of $a_2$, derivative d$\alpha$/d$T$, being the temperature profile, makes different visual impression than derivative d$\alpha_{eq}$/d$T$ followed from modified van't Hoff's isobar.

### Decomposition in dynamic conditions in vacuum

As follows from Table 2, high values of $a_2$=317–661 are the proof of crucial change of temperature profile according to Eq. (7):

$$\ln\alpha = a_0 - \frac{a_1}{T} \tag{12}$$

for three-parametric relationship (1):

$$\ln\alpha = a_0 - \frac{a_1}{T} - a_2 \ln T$$

Thus, relationship called temperature criterion [7, 13–18] describes, in the form of linear relationship (12), course of reaction/process for low, initial temperatures.

Equations (3) and (12) may be transformed in different way:

$$\alpha = C_1 \exp\left(-\frac{a_1}{T}\right),\quad C_1 = \exp(a_0) \tag{13}$$

as well according to Eq. (3):

$$\alpha = C_2 \left(\frac{T_f}{T}\right)^{a_2} \exp\left(-\frac{a_1}{T}\right) \tag{14}$$

where

$$C_2 = \exp\left(\frac{\alpha_1}{T_f}\right) \tag{15}$$

Fundamental relationship (13) in dynamic analysis, particularly when $\alpha=\alpha_{eq}$ is determined by the strength of variability $(T_f/T)^{\alpha_2}$. According to previously established properties, coefficient $a_2$ in Eqs (1), (3) and (5) is a measure of rate of reaction/process towards temperature, i.e. when $a_2$=0 – the thermodynamic relationship (7) is valid, and when $a_2$ is very high – one observes high decomposition rate. At the same time, according to Eq. (14), $a_2$ is a measure of thermodynamic relationship (7) deformation independently on temperature range.

### *Results of analyses for simulated decomposition of $CaCO_3$ according to Eq. (6)*

The aim of present considerations is presentation of relationships $\alpha$ *vs.* $T$ obtained from Eq. (6) and its constants (point 2 in 'Analyzed data') in the following way:

**I**. up to temperature $T=T_{eq}$=1157.4 K Eq. (6) was solved with the use of 4th order Runge–Kutta method,

**II**. for higher temperatures, $T>T_{eq}$ the following approximation was used [19, 20]:

$$g(\alpha) = \frac{AR}{qR}\frac{e^{-x}}{x}W(x) \tag{16}$$

where

$$x = \frac{E}{RT},\quad W(x) = \frac{x^3+18x^2+86x+96}{x^4+20x^3+120x^2+240x+120} \tag{17}$$

what can be presented as

$$g(\alpha) = \frac{AT}{q} e^{-\frac{E}{RT}} W\left(\frac{E}{RT}\right) \tag{18}$$

Results of calculations of connected data (**I**) and (**II**) were approximated with the use of Eq. (1) in order to find coefficients $a_0$, $a_1$ and $a_2$. The results are presented in Table 3, from which follows that for simulated thermal decomposition curves coefficient $a_2$ is very low ($a_2$<50), what virtually indicates equilibrium decomposition. Figure 2 presents simulated curves on the background of Eq. (7).

**Table 3** Estimation of coefficients from Eq. (1), significance level=0.0000

| n | $a_0$ | $a_1$ | $a_2$ | $R^2$ | $N$ | range $T$/K |
|---|---|---|---|---|---|---|
| 0 | 5.78 | 2.6526E4 | 1.869 | 1 | 64 | 800–1375 |
| 1/2 | 62.77 | 3.3636E4 | 5.344 | 0.9996 | 66 | 800–1420 |
| 1 | 145.49 | 4.4162E4 | 15.773 | 0.9974 | 65 | 800–1400 |
| 2 | 280.79 | 6.1613E4 | 32.811 | 0.9951 | 78 | 800–1750 |

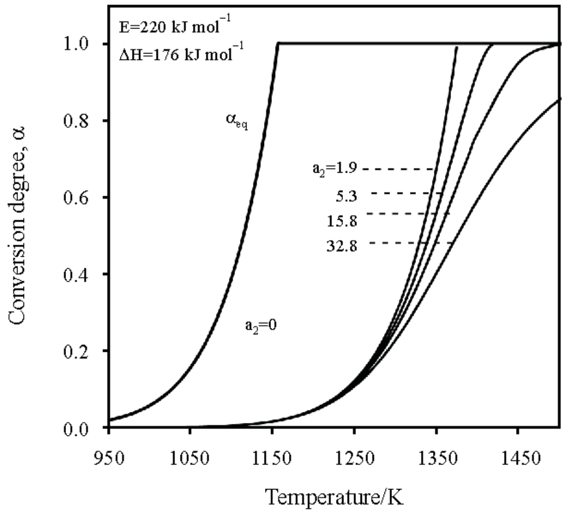

**Fig. 2** Simulated curves for decomposition of $CaCO_3$ (Table 3)

The paper by Czarnecki (on Fig. 3 in [21]) presents TG curves shift according to method of gaseous products reception, e.g. temperature of thermodynamic stability, procedure independent decomposition temperature, etc. These terms are often used in the qualitative description of thermal decompositions particularly when using variously closed crucibles common for derivatography and many become useful for other oriented authors. In case when $a_2 > 0$, kinetic factor in form of activation energy ($E$) appears instead of enthalpy ($\Delta H$).

### *Deviation from inequality (10)*

Analyzing values of maximal rates $(\mathrm{d}\alpha/\mathrm{d}T)_{\max}$ from Tables 1 and 2, particularly in vacuum (Table 2), there is a possibility of exceeding the postulated value for $CaCO_3$ ($v$=1) and $\alpha_{\mathrm{eq}}$=1:

$$\frac{\Delta H}{RT_{\mathrm{eq}}^2}=0.0158\ \mathrm{K}^{-1}$$

Results of thermal decomposition in vacuum (as well as under pressure of gaseous reaction product, $CO_2$) may be interpreted by Zawadzki–Bretsznajder law [22]. In case of analyses in vacuum two elements appear:

1) reaction becomes irreversible, because local sources of reversibility proposed by Maciejewski [23] are eliminated,

2) there is observed approaching of both temperatures: $T_f$ (for $\alpha$=1) as well as estimated $T^*=a_1/a_2$, while version of three-parametric Eq. (1) may be expressed by reduced form (3).

In the simplest understanding of observed facts, one may say that drastic reaction conditions caused by strong thermodynamic stimuli (here: vacuum) are expressed by deviations from standard thermodynamic laws, i.e. system reacts dynamically on equilibrium state shift.

In turn, it is worth considering opposite situation, when atmosphere is rich in gaseous product – in case of $CaCO_3$, thermogravimetric analyses were carried out in $CO_2$ atmosphere (point 4 in ‘Analyzed data’).

Results of these investigations are presented in form of classic Eq. (19) for $W(E/RT)=RT/E$. Calculation summary is presented in Table 4. The best results (albeit not satisfactory at all) were obtained for models DJ (Dahme–Junker [24] loc. cit. [25, 26]) and F1, and corrected values according to [27] lead to incredibly high activation energy $E$=1128.5/1362.9 kJ mol$^{-1}$, what is still consistent with Zawadzki–Bretsznajder law.

Next, Eqs (1) and (3) were used – Fig. 3a presents: experimental curve A together with estimated values from Eq. (1), curve B and rejected curve C – from Eq. (3).

It should be noticed that in relation to reference data (Tables 1 and 2), as well as, in this case, simulated data (Table 3), one must not be satisfied from estimation with the use of Eq. (1) – which does not include whole $\alpha$ variability range, and equation with imposed boundary condition (3) in turn leads to inadequate values of $\alpha$. In both cases coefficient $a_2$ is incredibly high.

**Table 4** Activation energy for DJ, F1, A2, A3, D3 models

| Model | $r^2$ | $E$/ kJ mol$^{-1}$ | Coefficient acc. [21] | $E_{\mathrm{corr}}$/ kJ mol$^{-1}$ |
|---|---|---|---|---|
| DJ | 0.9648 | 1362.9 | 1 | 1362.9 |
| F1 | 0.9504 | 1234.7 | 1 | 1234.7 |
| A2 | 0.9488 | 607.6 | 2 | 1215.2 |
| A3 | 0.9472 | 398.6 | 3 | 1195.8 |
| D3 | 0.9279 | 2257.0 | 1/2 | 1128.5 |

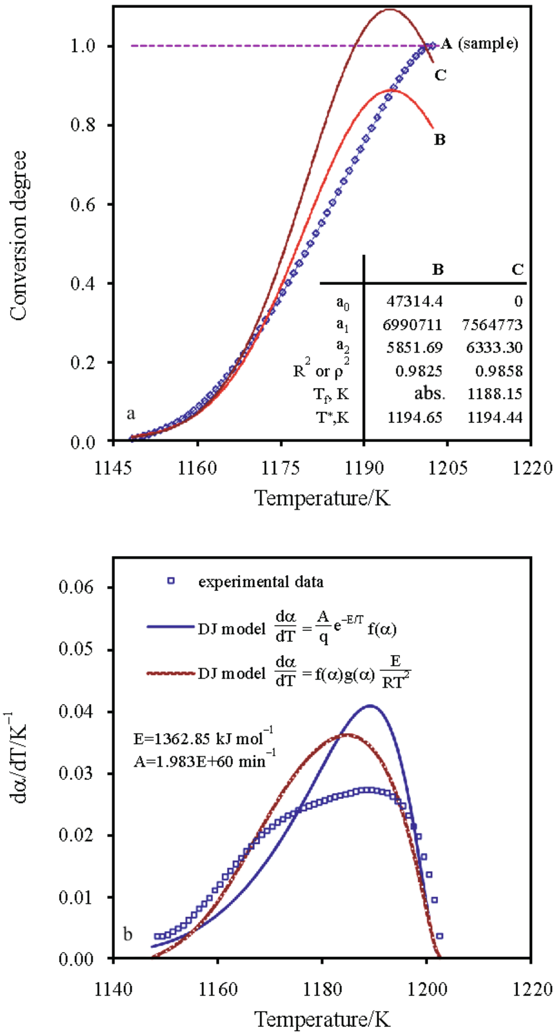

**Fig. 3** Relationship between the a – conversion degree ($\alpha$), b – reaction rate ($d\alpha/dT$) and temperature ($T$) for thermal dissociation of $CaCO_3/CO_2$ ($N$=56)

In the present work maximal reaction rate is the climax – apart from direct using of experimental data one may use two possibilities:

$$\frac{d\alpha}{dT}=\frac{A}{q}e^{-\frac{E}{RT}}f(\alpha)\text{ generalization of Eq. (6)} \tag{19}$$

and equation resulted from introduction of approximated solution (16), for $W(E/RT)=RT/E$, into Eq. (19):

$$\frac{d\alpha}{dT}=f(\alpha)g(\alpha)\frac{E}{RT^2} \tag{20}$$

In particular, when $T=T_m$, Eq. (20) may be presented in very interesting form:

$$\left(\frac{d\alpha}{dT}\right)_{T=T_m}=f(\alpha_m)g(\alpha_m)\frac{E}{RT_m^2} \tag{21}$$

For majority of functions $g(\alpha_m)=1$ [26], and component $f(\alpha_m)$ is generally well-known (i.e. [5]). Thus, one obtains:

$$\left(\frac{d\alpha}{dT}\right)_{T=T_m}=f(\alpha_m)\frac{E}{RT_m^2} \tag{22}$$

For best adjustment (function DJ) one obtains:

$$\left(\frac{d\alpha}{dT}\right)_{T=T_m}=\frac{1-\alpha_m}{1+\alpha_m}\left(\frac{E}{RT_m^2}\right) \tag{23}$$

and for $\alpha_m$=0.536 [26]:

$$\left(\frac{d\alpha}{dT}\right)_{T=T_m}=0.302\frac{E}{RT_m^2}=0.036\frac{E}{T_m^2} \tag{24}$$

Figure 3b presents relation between both derivatives: experimental and one according to Eqs (19) and (20).

On the other hand, for investigations in vacuum presented in [8] one may again use Eq. (22) – here, activation energy is lower than in case of atmospheric pressure, but temperature of maximal reaction rate decreases, thus derivative $d\alpha/dT$ increases (insignificantly), when $T=T_m$.

For incredibly high activation energies one may expect very high values of $d\alpha/dT$ at $T=T_m$. In case of atmosphere rich in gaseous product (here: $CO_2$) the thermodynamic stimulus, i.e. temperature, causes sudden decomposition. Thus, one may say that $CO_2$ excess is reaction inhibitor.

After using inequality (11) one may observe inequality sign reversion for very high values of $a_2$. Then, it may be a case that conversion degree from Eq. (1) does not reach value of $\alpha$=1, but below 1 ($\alpha$<1, Fig. 3a). Thus, one may assume that:

- if both Eqs (1) and (3) lead to very different estimations then, in spite of significance of Eq. (1) i.e. for very high values of $a_2$, three-parametric equation loses its meaning,
- probably in processes inhibited by gaseous products, evaluation of reaction/process kinetics in form of Eq. (7) for incredibly high activation energies in relation to thermodynamic considerations is also not valid,
- currently it is not known in what range coefficient $a_2$ reliably expresses accuracy of form Eq. (14).

Transforming Eq. (22) by dividing both sides by $\alpha_m$, one obtains:

$$r_m=\frac{f(\alpha_m)}{\alpha_m}\frac{E}{R},\text{ where }r_m=\frac{\left(\frac{d\alpha}{dT}\right)_{T=T_m}}{\alpha_m}T_m^2 \tag{25}$$

Equation (25) was derived with the use of different method – considering Kissinger law in [5] (Eq. (II-4) in [5]).

Thus, one may assume that deviations from inequality (10) may be explained by Eq. (22), which connects both theory expressed by Holba–Šesták equation and classic equations through interpretation of three-parametric Eqs (1) and (3) as well as Eqs (4) and (5) in Eq. (25).

### *Analysis of literature data and summary*

Coefficients of Eqs (1) or (3) were estimated with the use of literature data. Graphical representation of relationship:

$$a_1 = 37281.1+821.374a_2 \; (r^2=0.9980) \qquad (26)$$

is presented on Fig. 4 and was formed from following data:

- 4 results from Table 3,
- 7 results from Table 1,
- 6 results from Table 2,
- 2 results from [6] (Table 3 in [6]),
- 2 results from [28] for $q$=0.29 and 73.6 K min$^{-1}$ (also Table 3 in [6]),
- 1 result from [29],
- total $N$: 22 values.

Results for thermal decomposition of $CaCO_3/CO_2$ have been rejected, because of very high value of $a_2$.

In spite of accidental construction of data set, there is no question that linear relationship (19) postulated in [30, 31] is valid. It follows directly from Eq. (5), when one imposes condition to the straight-line to pass through the point of coordinates [$\Delta H/vR$; $T_r$], as it was presented in [25]. Finally:

$$r=\frac{\Delta H}{vR}+a_2(T_r-T) \qquad (27)$$

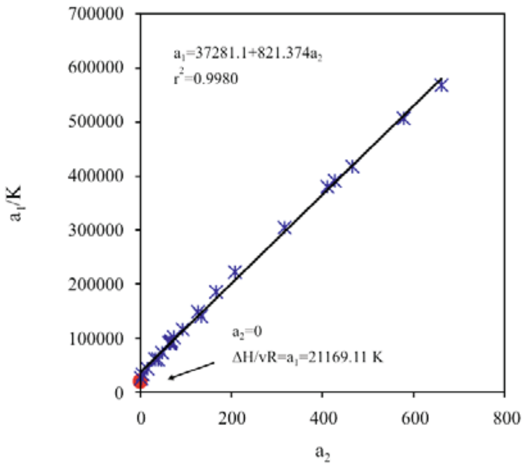

**Fig. 4** Relation between coefficients: $a_1$ *vs.* $a_2$

from which follows general form of Eq. (26):

$$a_1=\frac{\Delta H}{vR}+a_2T_r \qquad (28)$$

However, for $a_2$=0 one expects $a_1=\Delta H/vR$=21169.1 K, while obtained free term is much more higher. Nevertheless 95% prediction limit (significance level=0.05) includes postulated value. It is necessary to stress that discussed value for $a_2$=0 is dependent mainly on assumed average standard enthalpy, here $\Delta H$=176 kJ mol$^{-1}$.

Using Barin's tables [32] for calcite and for temperature range 298.15–1200 K one obtains:

$$\ln\alpha_{eq}=18.095-\frac{21039.57}{T} \qquad (29)$$

i.e. $\Delta H$=174.9 kJ mol$^{-1}$, $T_{eq}$=1162.7 K, thus constants are very close to the ones used in present work.

In older experimental works one can find also higher values of average enthalpy, e.g. $\Delta H$=187.7 kJ mol$^{-1}$ [33], and $\Delta H_{298}$=209.0 kJ mol$^{-1}$ [34] is very close to activation energy [8]. Even if one assumes $a_1=223\cdot10^3/8.314$=26461.39 K (Table 2 in [8]), the value is lower than obtained free term in linear relationship (19).

From mentioned work [33] (Fig. 1 in [33]) also follows $T_{eq}$=1058.2 K, what leads to value $\Delta H/RT_{eq}^2$=0.0202 K$^{-1}$ higher than it was given on Fig. 1.

## Discussion

### *Thesis I*

The work is composed of two elements, which are inseparable. The first thesis concerns comparison of maximal value of derivative $d\alpha_{eq}/d\underline{T}$, which in dynamic conditions for real samples transforms into maximal rate of reaction/process $d\alpha/dT$ at temperature $T_m$. Considerations presented in form (10) allow to conclude that rates of reaction/process towards temperature are lower (equal) than those resulted from thermodynamic considerations followed from modified van't Hoff's isobar (7). In dynamic conditions rate of reaction/process undergo deformation, starting from relationship:

$$\frac{d\alpha_{eq}}{dT}=\alpha_{eq}\frac{\Delta H}{vRT^2} \quad \text{for } T\le T_{eq} \qquad (30)$$

and

$$\frac{d\alpha_{eq}}{dT}=0 \quad \text{for } T\ge T_{eq}$$

to typical thermokinetic relationships, and a measure of the deformations is value of coefficient $a_2$, independently whether relation $\alpha<\alpha_{eq}$ for $p^0\cong0.1$ MPa=const. or reverse one occurs for variable pressure ($p$). From Eqs (4) and (5), as well as Eq. (14) one obtains:

$$\frac{d\alpha}{dT}=\alpha\left(\frac{a_1}{T^2}-\frac{a_2}{T}\right) \tag{31}$$

what in combination with theoretical relationship [30] of type (28) leads to expression:

$$\frac{d\alpha}{dT}=\alpha\left(\frac{\Delta H}{vRT^2}+a_2\frac{T_r-T}{T^2}\right) \tag{32}$$

Analyzing Eq. (32) one may find what is the quantitative influence of coefficient $a_2$ on above reaction rates. In Eq. (32) whole term in brackets disappears for $T=T_r$, and for $T>T_r$ the term changes its sign for '–', and for $T<T_r$ – remains '+'. In particular, the temperature range is connected with Holba–Šesták equation, what is the subject of previous work [5]. The considerations may suggest that for temperature $T_r$ derivative $d\alpha/dT$ reaches maximum, what is suggested that $T_r=T_m$. But it does not, what is presented in considerations initiated henceforth (Eqs (33)–(37)). Determining temperature $T_r$ from Eq. (28) one obtains:

$$T_r=\frac{a_1-\left(\frac{\Delta H}{vR}\right)}{a_2},\quad a_2\neq0 \tag{33}$$

Next, using Eq. (I-8) from [5] one obtains:

$$T_r=T_m\frac{1+a_2+\sqrt{1+a_2}}{a_2}-\frac{\Delta H}{vRa_2} \tag{34}$$

Equation (34) is also obtained from Eq. (32) for condition $d^2\alpha/dT^2=0$.

Using system approach, Eqs (32) and (34) may be considered for at least two possibilities:

a) $a_2=0$,
b) $a_2$ is very high.

In variant a) Eq. (32) without discussion transforms itself into Eq. (30) ($\alpha=\alpha_{eq}$).

Instead, in case b) starting from Eq. (34) for:

b1) e. g. $a_2>100$, because

$$\frac{1+a_2+\sqrt{1+a_2}}{a_2}=\sim1,\quad T_r<T_m \tag{35}$$

b2) from form (34) one obtains:

$$\lim_{a_2\to\infty}T_r=\lim\left(T_m\frac{1+a_2+\sqrt{1+a_2}}{a_2}-\frac{\Delta H}{vRa_2}\right) \tag{36}$$

that is:

$$T_r\to T_m \tag{37}$$

However, the crucial problem here is the fact, that inequality (35) is not maintained, so coefficient $a_2$ should not reach value of few thousands. It can be noted, that $T_r$=idem (Eqs (26) and (28)) but $T_m$=var when $q$=var.

Thus, conceptional comparison of Eqs (30) and (32) gives possibility of rate of reaction/process changes investigation in thermodynamic categories, i.e. towards temperature. From the course of presented analyses one may conclude that Thesis I, expressed by inequality (10), loses its meaning for processes, for which Zawadzki–Bretsznajder law is valid. Thermal decomposition in low pressure/vacuum manifests itself by decreasing of both temperature of maximal reaction rate and activation energy. Instead, process inhibited by increased partial pressure of gaseous product is distinguished i.e. by excessively high activation energy.

### Thesis II

In the light of considerations that have been carried out as well in this part, as in previous [12], analysis of thermal decomposition reaction/processes in dynamic conditions of type:

$$A(s)\leftrightarrow B(s)+vC(g) \tag{38}$$

or only towards gaseous products: $\Sigma vC(g)$, may be interpreted as thermodynamic disturbance presented in form (30) and controlled by the way the gaseous phase is created. According to symbolical Fig. 5, fast removal of gaseous products [$C(g)$] through vacuum generation, shifts real reaction/process rate curves on the left from basic relationship (7) or (29). In turn, in order to impede gaseous product evacuation (here: $CO_2$ atmosphere in case of carbonates or interaction of factors mentioned in works of Paulik *et al.* [35, 36]), curves shift right from isobaric relationship (7) or (29). Thus, observation of decomposition reaction is result of intentional or accidental selection of determination conditions not discussed in present work (heating rate, initial sample mass, sample purity, etc.). For analysis understood this way, occurrence of isokinetic/compensation effect [16, 19, 37–43] is very clear, because change of testing conditions (entropic part) causes activation energy variations. Occurrence of compensation effect in thermal dissociation reactions of many substances, as well as in biological processes or catalytic reactions, is well-known question [44–47]. Nevertheless, it is still brought on and is the subject of new publications [48, 49].

## Conclusions

Thermal decomposition of reference material $CaCO_3$ as well in nitrogen, as in vacuum – which was subject of

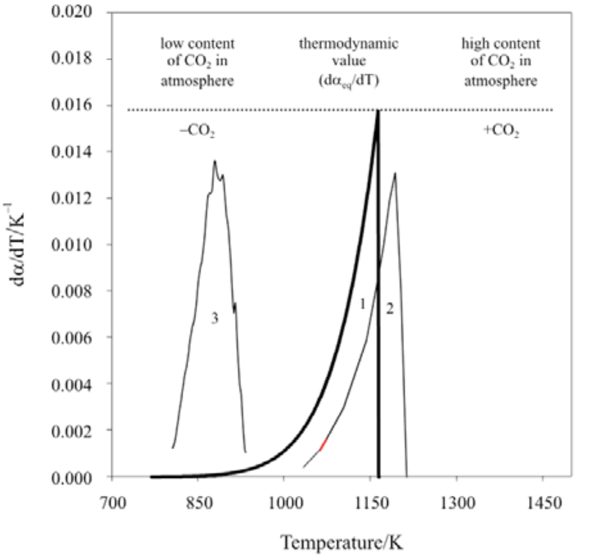

**Fig. 5** Relationship between the reaction rate (d$\alpha$/d$T$) and temperature ($T$) for thermal dissociation of $CaCO_3$: 1 – thermodynamic value (d$\alpha_{eq}$/d$T$), 2 – analysis in the air (Fig. 2, No. 1 in [6]), 3 – decomposition of $CaCO_3$ in vacuum (Table 2, $q$ = 6.2 K min$^{-1}$)

works recapitulating ICTAC Kinetic Project (1996) [8–11] – was described with the use of three-parametric equation in version (3). The form includes two parameters ($a_1$ and $a_2$) and imposed temperature condition $T_f$ (final state), for which $\alpha$=1. After transformation of Eq. (3) into form (14) it appears the influence of temperature simplex and exponent $a_2$, thus $[(T_f/T)^{a_2}]$ as the value directly proportional to conversion degree ($\alpha$). The higher is coefficient $a_2$, the stronger is deformation of the basic relationship in analysis of thermal decomposition presented by expression: exp($-a_1/T$). According to previous settlements coefficient $a_2$ in Eqs (1), (3) and (5) is of kinetic nature. For $a_2$=0 and for individual pure chemical compounds thermodynamic relationship (7) is correct. Thus, it is as well measure of rate of reaction/process towards temperature, as deformation of the basic relationship (7) independently on temperature range understood as a location towards equilibrium temperature profile $\alpha_{eq}$ *vs.* $T$ for $p^0$=const.

It was established that in three-parametric Eqs (1), (3) or (5) coefficients $a_1$ and $a_2$ are linearly correlated according to formula (28). The correlation was verified for different data – reference, simulated, own and literature. Instead, for $a_2$=0 coefficient $a_1$ reaches minimal value of thermodynamic character ($\Delta H/\nu R$). However, the relationship forces to think that the kinetic aspect expressed by coefficient $a_2$ must have limitations, following from considerations expressed by Eqs (27), (32)–(34). Thus, very high values of $a_2$, of order of few thousands, cause that three-parametric Eqs (1) and (3) approximates only the beginning of reaction/process pathway (Fig. 3a).

The consequence of Holba–Šesták equation (Eq. (5) in [5]) is inequality (10) valid for conditions not included by Zawadzki–Bretsznajder law. Thermal decomposition in vacuum manifests itself in decrease of temperature of maximal reaction/process rate as well as activation energy. Instead, process inhibited by increased partial pressure of formed gaseous products is distinguished by i.e. excessively high activation energy.

In the light of [5] and this paper, estimation of basic parameters of Arrhenius law in connection with kinetic function, so called single kinetic triplet:

$$f(\alpha)\text{–}E\text{–}A \quad \text{or} \quad g(\alpha)\text{–}E\text{–}A$$

without analytical normalization of reaction/process conditions (particularly how to treat gaseous products), is information very difficult to reconstruct in different conditions. One of possibilities of uncontrolled conditions influence is analysis at different heating rates ($q$=var). It may be enabled by using of isoconversional methods [50–53]. Thus, the question of function $f(\alpha)$ selection is omitted and one concentrates on basic aim of energy activation ($E$) estimation and on further consequences (e.g. next estimation pre-exponential factor in Arrhenius equation ($A$)).

## Nomenclature

| | |
|---|---|
| $a_0$, $a_1$ and $a_2$ | coefficients of three-parametric equation, acc. to Eq. (1) |
| $A$ | pre-exponential factor in Arrhenius equation, min$^{-1}$ (or s$^{-1}$) |
| $E$ | activation energy, J mol$^{-1}$ |
| $f(\alpha)$ and $g(\alpha)$ | kinetic functions of conversion degree $\alpha$ |
| $\Delta H$ | enthalpy, J mol$^{-1}$ |
| $n$ | reaction order |
| $p$ | pressure, Pa |
| $p^0$ | standard pressure, $p^0 \cong 0.1$ MPa |
| $q$ | heating rate, K min$^{-1}$ (or K s$^{-1}$) |
| $r$ | relative rate of reaction/process, K |
| $R$ | universal gas constant, $R$=8.314 J mol$^{-1}$ K$^{-1}$ |
| $T$ | temperature, K |
| $T_{eq}$ | equilibrium temperature for $\alpha_{eq}$=1 at pressure $p^0 \cong 0.1$ MPa, K |
| $T_r$ | temperature – slope in Eq. (28) (remarks in [19]), K |
| $T^*$ | temperature for which $r$=0 in Eq. (5), K |

*Statistical symbols:*

| | |
|---|---|
| $N$ | number of data |
| $r^2$ | determination coefficient for linear function, $0 \le r^2 \le 1$ |
| $R^2$ | multiplicative determination coefficient, $0 \le R^2 \le 1$ |
| $\rho^2$ | multiplicative determination coefficient without intercept, $0 \le \rho^2 \le 1$ |

*Subscripts:*

| | |
|---|---|
| eq | equilibrium state |
| *f* | final state |
| *m* or max | point of the maximal rate of reaction/process |

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