Journal of Thermal Analysis and Calorimetry, Vol. 74 (2003) 433–442

# THERMODYNAMIC INTERPRETATION OF THREE-PARAMETRIC EQUATION
# Part II. The relative rate of reaction

*A. Mianowski* [1*] *and R. Bigda* [2]

[1]Department of Chemical Technology of Coal and Petroleum, Silesian University of Technology, 44-100 Gliwice, Krzywoustego 8, Poland
[2]Institute for Chemical Processing of Coal, 41-803 Zabrze, Zamkowa 1, Poland

## Abstract

The way of practical using of three-parametric equation transformed into linear relation between relative rate of decomposition and temperature was presented, basing on thermal decomposition of chemically defined and other compounds. Further possibilities of interpretation of that relation were presented. The meaning of slope ($a_2$) was laid down, particularly with connection to thermodynamic considerations.

**Keywords:** coefficient $a_2$, correlations, $CuSO_4 \cdot 5H_2O$, relative rate of thermal decomposition, solid paraffin, three-parametric equation

## Introduction and aim of the work

Using of three-parametric Eq. (1):

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

and linear Eq. (2) of relative rate of reaction of thermal decomposition ($r$) *vs.* temperature ($T$) in dynamic conditions, which follows from Eq. (1):

$$r = a_1 - a_2 T \tag{2}$$

is the object of considerations continuing the investigations presented in [1].

The relationship [2]:

$$r = -\frac{\mathrm{d}\ln\alpha}{\mathrm{d}(1/T)} = -\frac{\Delta\ln\alpha}{\Delta(1/T)} \tag{3}$$

has been chosen from three different possibilities of value $r$ determination. Above-mentioned relationships minimize deviations from straight-line (2), which appear in initial stage of reaction of decomposition (e.g. Fig. 4 in [2]).

---

* Author for correspondence: E-mail: miano@polsl.gliwice.pl

1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

The aim of the work is to prove, how pertinently do the coefficients of Eq. (1) describe Eq. (2) in dynamic conditions (heating rate $q>0$) in case of chemically defined compounds. For this purpose thermal decomposition of $CuSO_4 \cdot 5H_2O$, which was analyzed in previous work [3] and in [1], has been considered.

## Analysis of the problem

From papers published up to now [4–6] results that connecting Eqs (1) and (2) is very good for thermal decomposition of such chemically complicated substances, as: coal [4], coal tar pitch [5], mixtures of polyolefines with technological oil [6]. So the chemical compound $CaC_2O_4 \cdot H_2O$ (three sequential reactions) discussed in [2] should be completed with another ones.

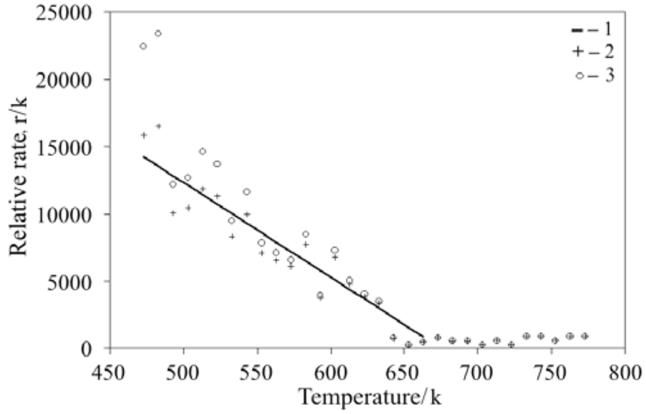

**Fig. 1** Thermal decomposition of solid paraffin (+ – experimental data from [7]): 1) $r=4.75 \cdot 10^{-4}-70.33T$ ($R^2=0.9990$, when acc. Eq. (1) $a_0=528.58$); 2) $r$ determined by Eq. (3), $R_1^2=0.8569$; 3) $r=-[\Delta m/\Delta T\,(m_i-m)]T^2$, $R_1^2=0.6075$

In other way, by comparing two methods of determining $r$ (Fig. 1) one proved that Eq. (3) is more profitable than another very convenient possibility ($r=-[DTG/(m_i-TG)]T^2$, where: $m_i$ – initial mass).

The determination coefficient given in caption of Fig. 1 has been related to straight-line (2) and to coefficients of Eq. (1):

$$R_1^2 = 1 - \frac{\sum [r - r_{\text{acc.}(2)}]^2}{\sum' r^2} \tag{4}$$

where $r$ is described by formula (3), and ′ is an operator proposed by Volk [8].

Formula (3) has been taken for further analysis.

## Results

Thermal decomposition of $CuSO_4\cdot 5H_2O$ ($q$=1.5–3–6–12 and 24 K min$^{-1}$) according to scheme: $A^{(s)}\leftrightarrow B^{(s)}+\nu C^{(g)}$ has been analyzed. The data investigated have formed 25 graphic illustrations of *r vs. T* relationship with number of 10–50 points (depending on reaction).

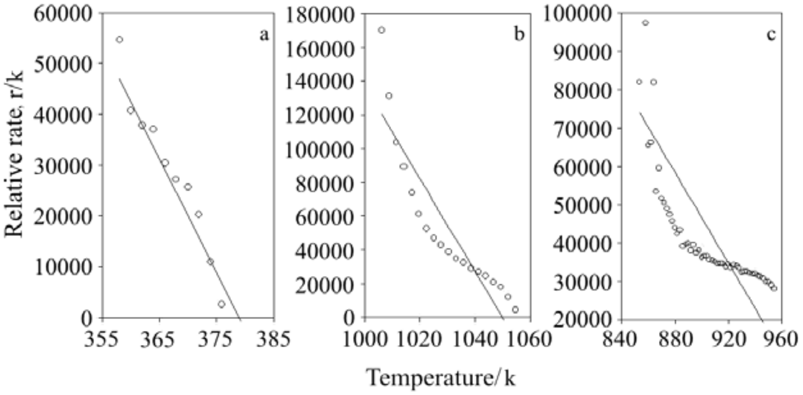

**Fig. 2** Three cases of relation of relative rate of reaction of decomposition *vs*. temperature (3) with reference to linear relation (2) for decomposition of $CuSO_4\cdot 5H_2O$: a – correlation $R_1^2>0.90$ (reaction Ib, $q$=1.5 K min$^{-1}$), $R_1^2=0.9255$; b – correlation $0.50<R_1^2<0.90$ (reaction IIIb, $q$=6 K min$^{-1}$), $R_1^2=0.6532$; c – correlation $R_1^2<0.50$ (reaction IIIa, $q$=1.5 K min$^{-1}$), $R_1^2=0.3062$

There are values of determination coefficient $R_1^2$ according to relationship (4) for 5 heating rates and for 5 reactions in Table 1. Figure 2 presents three chosen graphical relationships of relative rate of reaction *vs.* temperature, comprising two extreme cases (Figs 2a and c).

## Discussion

As Table 1 and Fig. 2 show, basing on experimental material for considered reactions of thermal decomposition of $CuSO_4\cdot 5H_2O$, we can not mark out closely connected relations between coefficients $a_1$ and $a_2$ of Eq. (1) used in Eq. (2) assuming that we profit from formula (3) and determination coefficient (4).

For explaining this question we use Eq. (1) in form (Eq. (10) in [1]):

$$\ln\alpha=\ln\alpha_{\mathrm{eq}}-a_2\left(\frac{T_{\mathrm{r}}}{T}+\ln T-\gamma\right),\qquad q=\mathrm{var} \tag{5}$$

After differentiating with regard to temperature and after multiplying by $T^2$, we obtain:

**Table 1** Comparison of $R_1^2$ coefficients for individual reactions of $CuSO_4 \cdot 5H_2O$ decomposition for 5 heating rates *q*

| Reaction | | ν | $R_1^2$ for $q$/K min$^{-1}$ | | | | |
|---|---|---|---|---|---|---|---|
| | | | 1.5 | 3 | 6 | 12 | 24 |
| Ia | $CuSO_4 \cdot 5H_2O{=}CuSO_4 \cdot 3H_2O{+}2H_2O$ | 2 | 0.7841 | 0.8943 | 0.8346 | 0.8102 | 0.7732 |
| Ib | $CuSO_4 \cdot 3H_2O{=}CuSO_4 \cdot H_2O{+}2H_2O$ | 2 | 0.9255 | 0.9007 | 0.8808 | 0.8131 | 0.7567 |
| II | $CuSO_4 \cdot H_2O{=}CuSO_4{+}H_2O$ | 1 | 0.7844 | 0.7023 | 0.6727 | 0.6843 | 0.6661 |
| IIIa | $2CuSO_4{=}CuO \cdot CuSO_4{+}SO_3$ | 1 | 0.3062 | 0.3559 | 0.3885 | 0.4067 | 0.3631 |
| IIIb | $CuO \cdot CuSO_4{=}2CuO{+}SO_3$ | 1 | 0.4717 | 0.6466 | 0.6532 | 0.6481 | 0.6236 |

$$r=\frac{\mathrm{d}\ln\alpha_{\mathrm{eq}}}{\mathrm{d}T}T^{2}-a_{2}(T-T_{\mathrm{r}}) \tag{6}$$

where the first expression on right-hand side is equal to $r_{\mathrm{eq}}=\Delta H/\nu\mathrm{R}(\mathrm{d}\ln\alpha_{\mathrm{eq}}/\mathrm{d}T=$ $=\Delta H/\nu RT^{2})$. Finally we obtain identical formula (Eq. (8) in [1]):

$$r=r_{\mathrm{eq}}-a_{2}(T-T_{\mathrm{r}}) \tag{7}$$

In [2] one confirmed that:

$$r=a_{2}(T^{*}-T),\text{when } T^{*}=T,\text{ then } r=0 \tag{8}$$

and finally the situation presented on Fig. 3 occurs (line 1). Thus, another possibility of coefficient $a_2$ defining arises from comparison of relationships (7) and (8).

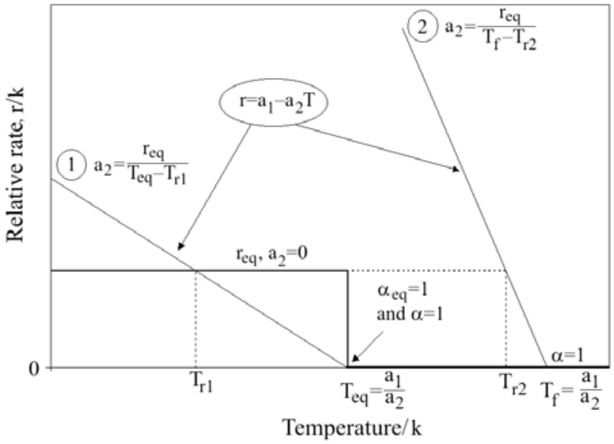

**Fig. 3** Idealized relations of relative rate of reaction of thermal decomposition *vs*. temperature

It is known from investigations [1] that heating rate $q$ has very big influence on coefficient $a_2$ ($a_2>0$). Thus, if there would be no restrictions of thermodynamic nature, then all linear relationships (2) should intersect in point with coordinates $[r_{\mathrm{eq}},T_{\mathrm{r}}]$. So $T_{\mathrm{r}}$ is temperature of intersection of bunch of straight-lines $r$, only when $T_{\mathrm{r}}$=idem for $q$=var.

Nevertheless, theoretically the second point with coordinates $[0,T^{*}]$ appears according to Eq. (8) and this condition causes that in relation to temperature, in which we take$\alpha_{\mathrm{eq}}=1$, from the bunch only one straight-line remains:

$$r=r_{\mathrm{eq}}\frac{T^{*}-T}{T^{*}-T_{\mathrm{r}}}=\frac{\Delta H}{\nu R}\frac{T^{*}-T}{T^{*}-T_{\mathrm{r}}} \tag{9}$$

At last, regarding to Eq. (5) in [1] we have:

$$\text{when } \alpha_{\mathrm{eq}}=1,\text{ then } T_{\mathrm{eq}}=T^{*} \tag{10}$$

and we obtain Eq. (9) in form:

$$r = \frac{\Delta H}{\nu R} \frac{T_{eq} - T}{T_{eq} - T_{r1}} \tag{11}$$

From Eq. (11) follows that in particular case ($a_2 = r_{eq}/(T_{eq} - T_{r1})$) relative rate of reaction of thermal decomposition (with temperature dimension) is the product of thermodynamic nature component and dimensionless temperature difference simplex. From Eq. (9) follows another possibility of description of linear dependence presented on Fig. 3 (line 2):

$$r = r_{eq} \frac{T_f - T}{T_f - T_{r2}}, \quad T_f = \frac{a_1}{a_2} \tag{12}$$

which interpretation is identical as for Eq. (11).

Comparing forms (11) and (12) the first one seems to be privileged, because it is consisted of three strictly thermodynamically defined quantities ($\Delta H$, $T_{eq}$ and $\nu$) however the meaning of empirically calculated temperature $T_r$ is indeterminate. The changeability ranges of these temperatures may also be assumed as: $0 \le T_{r1} < T_{eq}$ and $T_{eq} \le T_{r2} < T_f$ (symbols are explained on Fig. 3). Thus, it is interesting what form of (1) we obtain originating from Eq. (11). After separation of variables we have:

$$\int_{\alpha}^{1} \frac{d\alpha}{\alpha} = \frac{\Delta H}{\nu R (T_{eq} - T_{r1})} \left( T_{eq} \int_{T}^{T_{eq}} \frac{dT}{T^2} - \int_{T}^{T_{eq}} \frac{dT}{T} \right) \tag{13}$$

and finally

$$\ln\alpha = \frac{\Delta H}{\nu R (T_{eq} - T_{r1})} \left( 1 - \frac{T_{eq}}{T} + \ln \frac{T_{eq}}{T} \right), \quad T = T_{eq}, \quad \alpha = 1 \tag{14}$$

Equation (14) may be transformed using van't Hoff's isobar (Eq. (5) in [1]) and presented in form:

$$\ln\alpha = C \left( \ln\alpha_{eq} + \frac{\Delta H}{\nu R T_{eq}} \ln \frac{T_{eq}}{T} \right), \quad q = \text{var} \tag{15}$$

where

$$C = \frac{T_{eq}}{T_{eq} - T_{r1}}, \quad T_{eq} > T_{r1}, \quad 1 \le C < \infty \tag{16}$$

and then

$$\ln\alpha = C \ln\alpha_{eq} + a_2 \ln \frac{T_{eq}}{T} \tag{17}$$

or

$$\alpha = a_{\mathrm{eq}}^{\mathrm{C}} \left( \frac{T_{\mathrm{eq}}}{T} \right)^{\alpha_2} \tag{18}$$

where (Fig. 3 line 1)

$$a_2 = \frac{r_{\mathrm{eq}}}{T_{\mathrm{eq}} - T_{\mathrm{r1}}} = \frac{\Delta H}{\nu R (T_{\mathrm{eq}} - T_{\mathrm{r1}})} = C \frac{\Delta H}{\nu R T_{\mathrm{eq}}} \tag{19}$$

The temperature analyzed ($T_{\mathrm{r1}}$) appears in $C$ constant only. Let us observe that full conformity with Eq. (5) will ensue when $T_{\mathrm{r}}=0$ and $a_2=0$ simultaneously. In other words, Eq. (17) may present relationships different than three-parametric equation in version (1) or in (5).

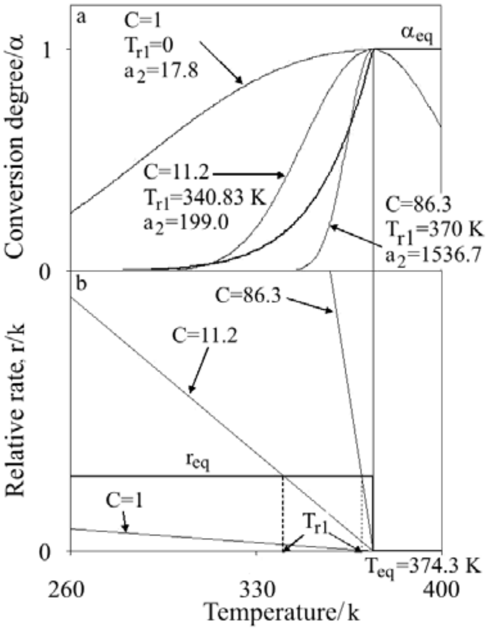

**Fig. 4** Three cases of relation (17) for first stage of thermal decomposition of $CuSO_4{\cdot}5H_2O$ (reaction Ia in Table 1) on the background of equilibrium line for the lowest, for high value of $C$ and for $C$ corresponding to $T_{\mathrm{r1}}$=340.83 K (Eq. (7) and Fig. 3 in [1]): a – α *vs.* $T$ relation; b – $r$ *vs.* $T$ relation

The chosen relationships (17) for freely selected $C$ constants and thus, $T_{\mathrm{r1}}$ (Fig. 4a) are presented against the background of α *vs.* $T$ relationship for reaction Ia (Table 1). From Fig. 4a follows that Eq. (17) determines experimental curves α *vs.* $T$ with totally dissimilar interpretation than it is given in [9] for Eq. (1). Variable temperature $T_{\mathrm{r1}}$ along with $r$ *vs.* $T$ straight-line intersection point [0,$T_{\mathrm{eq}}$] (Fig. 4b) generate three-parametric Eq. (1) with coefficients incoherent with prevailing state of knowledge about their meaning. It means that temperature $T_{r1}$ may be equal $T_{r2}$ (line 2 on Fig. 3) or even $T_{r3}$ by modifying Eq. (12) to form:

$$r=r(T_{r3})\frac{T_f-T}{T_f-T_{r3}},\ r(T_{r3})\neq r_{eq} \tag{20}$$

on the basis of Eqs (7) and (8). Theoretically, relation (2) should generate straight-lines intersecting in point $[r_{eq},T_{r1}]$, but using experimental data we observe the point of intersection in other location $[r(T_{r3}),T_{r3}]$ (Fig. 5).

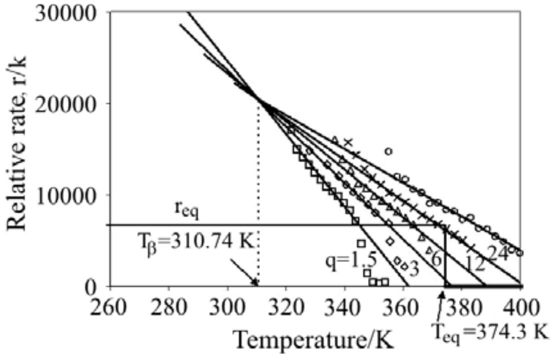

**Fig. 5** Relations of relative rate of reaction of thermal decomposition *vs.* temperature for 5 heating rates for thermal decomposition of $CuSO_4{\cdot}5H_2O$ (reaction Ia in Table 1). Straight-lines represent linear approximations for points corresponding to straight-line segment of $r$ *vs.* $T$ relation

Thus, temperature $T_r$ has either empirical or closely connected with temperature profile $r_{eq}$ *vs.* $T$ (Eq. (12)) or independent character (Eq. (20)). Analysis of cases expressed by Eqs (11) to (20) made possible widening of meaning of three-parametric Eq. (1). Thanks to the sequence: Eq. (1), after differentiation – Eq. (2), after integration – Eq. (1) again, the arguments strengthening the thermodynamic interpretation of basic Eq. (1) analyzed in Part I [1] were obtained.

## Conclusions

- One confirms that relation of relative rate of reaction *vs.* temperature presented by formula (3) determine coefficients of straight-line (2), what is presented by thermal transformation of paraffin (Fig. 1). Nevertheless, values of determination coefficient may vary in wide range ($0.31<R_1^2<0.92$) in case of decomposition of chemically defined compounds (for instance: $CuSO_4{\cdot}5H_2O$).
- Using Eq. (1) in form (5) relation (2) appears in form (7) which determine meaning of coefficient $a_2$ in other way. And the next, originating from Eq. (11) one may obtain Eq. (1) in another form (17) containing equilibrium conversion degree ($\alpha_{eq}$) and only one of three coefficients ($a_2$), which is now expressed by constant $C$ de-

pendent on temperature $T_{r1}$. Nevertheless Eq. (17) may present other relations than Eq. (1) or (5).

- Only equation containing temperature $T_{r1}$ (11) is privileged, because it contains three strictly thermodynamically defined quantities ($\Delta H$, $T_{eq}$ and $\nu$). However it is still hard to say what is the meaning of slope $T_r$ in Eq. (7) in [1].

## Symbols

| | |
|---|---|
| $a_1$, $a_2$, $a_3$ | coefficients of three-parametric equation, acc. Eq. (1) |
| $\alpha$ | conversion degree, $0 \le \alpha \le 1$ |
| $C$ | auxiliary dimensionless quantity defined by Eq. (16); $1 \le C < \infty$, |
| $\gamma$ | slope in Eq. (6) in [1], |
| $\Delta H$ | enthalpy/J mol$^{-1}$, |
| $m$ | mass/mg, |
| $\nu$ | stoichiometric coefficient, |
| $q$ | heating rate/K min$^{-1}$, |
| $r$ | relative rate of reaction of thermal decomposition/K, |
| $R^2$, $R_1^2$ | determination coefficient, ($R_1^2$ acc. Eq. (4)), $0 \le R^2$ or $R_1^2 \le 1$, |
| $R$ | gas constant, 8.314 J mol$^{-1}$ K$^{-1}$, |
| $T$ | temperature/K, |
| $T_r$ | slope in Eq. (7) in [1]/K, |
| $T^*$ | maximum of function which results from transformation of Eq. (1)/K; $d\alpha/dT=0$. |

*Subscripts*

| | |
|---|---|
| eq | equilibrium state, |
| i, f | initial and final state, respectively. |

*Superscripts*

| | |
|---|---|
| ($s$), ($g$) | solid and gaseous state, respectively. |

## References

1 A. Mianowski and R. Bigda, J. Therm. Anal. Cal., 74 (2003) 423.
2 A. Mianowski, J. Therm. Anal. Cal., 63 (2001) 765.
3 A. Mianowski and R. Bigda, J. Therm. Anal. Cal., 2003 (in press).
4 A. Mianowski, Some remarks on the nature of thermogravimetric profiles of bituminous coal, WSKKTCh, TECHEM III, pp. 527–530 Gliwice 2000 (in English).
5 A. Mianowski, S. Błażewicz and Z. Robak, Carbon, 2003 (in press).
6 A. Mianowski and T. Siudyga, J. Therm. Anal. Cal., 74 (2003) 623

7 T. Radko, Department of Chemical Technology of Coal and Petroleum, Silesian University of Technology, Gliwice, unpublished data (at Author’s).
8 W. Volk, Applied Statistics for Engineers, McGraw-Hill Book Co., 1958.
9 A. Mianowski, J. Therm. Anal. Cal., 59 (2000) 747.