THERMODYNAMIC INTERPRETATION OF THREE-PARAMETRIC EQUATION
Part I. New form of equation

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Abstract

Thermodynamic interpretation of three-parametric equation connecting conversion degree (α) with temperature (T) was presented. One proved that thermal decomposition process of chemically defined compounds ($CuSO_4 \cdot 5H_2O$, $PhN(CH_3)_2 \cdot HCl$) in dynamic conditions for 5 heating rates may be described by transformed three-parametric equation including equilibrium conversion degree.

Keywords: conversion degree, equilibrium conversion degree, thermal decomposition, three-parametric equation

Introduction

The kinetic investigations of linear temperature increase *vs.* time (with heating rate $q>0$) in dynamic conditions are still arouse great interest. The series of papers recapitulating the results of the 11th International Congress of Thermal Analysis and Calorimetry (ICTAC) in Philadelphia in 1996 [1–5] can show about that.

These very complicated but fascinating kinetic and thermodynamic problems have been appearing in literature many times, except work of MacCallum and Tanner in 1970 [6] which started the discussion on thermokinetic equations, the universal equation of Šesták *et al.* [7, 8] or considerations of Błażejowski *et al.* [9–11] or others [12] must also be taken into consideration.

The aim of the work

On St. Bretsznajder's 7th Seminar in Zakopane (Poland) the conception of relation between conversion degree (α) and temperature (T) was presented in form of three-parametric equation:

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

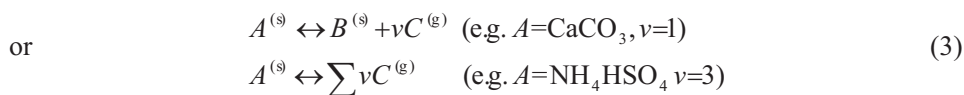*   Author for correspondence: E-mail: miano@polsl.gliwice.pl

which is more widely discussed in [13]. Then, using of this equation was proposed in form of relation between relative rate of reaction of thermal decomposition (r) and temperature (T) [14]:

$$r=a_1-a_2T, \text{ where } r=\frac{\mathrm{d}\alpha}{\alpha\mathrm{d}T}T^2 \tag{2}$$

From papers published up to now results that Eq. (2) is very useful for analyzing the reactions of thermal decomposition of complicated mixtures, as: transformation of coal tar pitch into mesophase one [15] or transformation of triple component system, polyolefines-technological oil-mineral additive, into fuel fractions [16].

Very important meaning of coefficient a_2 (with kinetic character) and its criterional character come true in all considerations [13–17]. When $a_2=0$, then relations (1) and (2) simplify themselves considerably and present thermodynamic description, because $\alpha=\alpha_{eq}$.

Therefore, the aim of the work is widening interpretation capabilities of Eqs (1) and (2) for chemical reactions which take into consideration stoichiometric coefficient v:

$$A^{(s)} \leftrightarrow B^{(s)}+vC^{(g)} \quad (\text{e.g. } A=CaCO_3, v=1)$$

or

$$A^{(s)} \leftrightarrow \sum vC^{(g)} \qquad (\text{e.g. } A=NH_4HSO_4\ v=3) \tag{3}$$

Theoretical analysis of the problem

For chemical reactions (3) the thermodynamic equilibrium constant is presented by expression [13, 18–21]:

$$K=\alpha_{eq}^{v}, \qquad p^{\circ}\cong 0.1\,\mathrm{MPa} \tag{4}$$

so, the modified van't Hoff's isobar may be presented in form including enthalpy of decomposition (ΔH):

$$\ln\alpha_{eq}=-\frac{\Delta H}{vRT}+\frac{\Delta H}{vRT_{eq}}, \quad \text{when } T=T_{eq}\ \alpha_{eq}=1 \tag{5}$$

so, for $T\geq T_{eq}$ reactions of type (3) become irreversible.

Taking changeable heating rates ($q=1.5-3-6-12$ and $24\ \mathrm{K\ min}^{-1}$), extremely important correlation between all coefficients of Eq. (1) has been confirmed in our investigations. Therefore, elements of linear determination coefficients square matrix are practically greater than $+0.99$ (component of a diagonal is equal to 1) thus, for assumed hierarchy of importance with regard to argument a_2, we obtain:

$$a_0=a_{0.0}+\gamma a_2, \qquad a_{0.0}=\frac{\Delta H}{vRT_{eq}}=\frac{r_{eq}}{T_{eq}} \left.\begin{array}{c} \\ \\ \end{array}\right\} \tag{6}$$
$$a_1=a_{0.1}+T_{r}a_2 \qquad a_{0.1}=\frac{\Delta H}{vR}=r_{eq} \quad q=\mathrm{var} \tag{7}$$

In many cases free expressions in Eqs (6) and (7) have differed numerically from these given by Eq. (5), in spite of very important correlation. Slopes in Eq. (6) vary insignificantly, $\gamma=6.83–7.92$. But very small deviations (as small as on the first place after comma) cause very altered courses of inquired new form of Eq. (1). On the other hand, in case of Eq. (7) the slope means temperature T_r. Introducing this equation into (2) we obtain:

$$r = \frac{\Delta H}{vR} - a_2(T-T_r) = r_{eq} - a_2(T-T_r) \tag{8}$$

For $a_2>0$ ($a_2=0$, then $r=r_{eq}$) straight-line (8) intersects parallel-line $r=r_{eq}$ in point T_r, so there is a straight-line bunch (2) intersecting in this temperature, too. This analysis is the subject of parallel publications [16, 17].

Introducing straight-lines (6) and (7) into Eq. (1) we obtain:

$$\ln\alpha = a_{0.0} - \frac{a_{0.1}}{T} - a_2\left(\frac{T_r}{T} + \ln T - \gamma\right) \tag{9}$$

what we can write using expression (5) as:

$$\ln\alpha = \ln\alpha_{eq} - a_2 f(T), \qquad \text{where } f(T) = \frac{T_r}{T} + \ln T - \gamma \tag{10}$$

Relationship (10) is inquired transformation of Eq. (1).

Introducing the idea of thermodynamic yield η we obtain:

$$\ln\left(\frac{\alpha}{\alpha_{eq}}\right) = \ln\eta = -a_2 f(T) \qquad 0 < \eta \leq 1 \tag{11}$$

The deviations from equilibrium state (5) may be explained by coefficient a_2 and temperature function $f(T)$. When $a_2=0$, then equilibrium state is in force for reaction (3).

When $a_2>0$, then we have such possibilities, as:

- $f(T)>0$, then clear deviation of conversion degree α *vs.* T takes place on the right from Eq. (5),
- $f(T)=0$, then α *vs.* T curve intersects course of curve (5) in one point; consequently: $\gamma = \frac{T_r}{T_{eq}} + \ln T_{eq}$ when $\alpha = \alpha_{eq} = 1$ in $T=T_{eq}$,
- $f(T)$ has two zeros, so α *vs.* T intersects the course twice,
- $f(T)<0$, then α *vs.* T curve goes over curve (5) – widened analysis of such observation with regards to pressure influence ($dp<0$) is necessary here, because $\eta=\alpha/\alpha_{eq}\geq1$.

The temperature function $f(T)$ should be independent from heating rate q in Eqs (9) to (11).

Experimental analysis of the problem

There have been many chemical compounds analyzed during our investigations, but presentation of results was restricted to two reactions:

$$CuSO_4 \cdot 5H_2O = CuSO_4 \cdot 3H_2O + 2H_2O \ (v=2) \tag{12}$$

$$PhN(CH_3)_2 \cdot HCl = PhN(CH_3)_2 + HCl \ (v=2) \tag{13}$$

Closer investigations of thermal decomposition of $CuSO_4 \cdot 5H_2O$ were presented in [22] and choice of amine (13) has been suggested by results of [20].

Thermal decomposition of copper sulphate pentahydrate (Thermal Analysis Tutorial Kit, ME-29710, Mettler TA-Test Sample) has been carried over using Mettler TG-50 thermobalance in TA-4000 thermoanalytic system, for weight samples of 20 ± 0.01 mg, in nitrogen (200 ml min^{-1}) in platinum crucible (open) for 5 heating rates.

N,N-dimethyl-aniline hydrochloride has been obtained as a result of reaction between gaseous HCl with N,N-dimethyl-aniline, according to [23]. Preparation of this compound has been consisted of two stages: in the first one, the solution of gaseous HCl has been made in anhydrous diethyl ether; in the second one, the prepared solution of HCl has been being added into N,N-dimethyl-aniline during continuous mixing of the reagents. Precipitated hydrochloride crystals have been dried. Melting point of obtained compound has amounted to $t_m = 68–73°C$ (according to [23], $t_m = 85–95°C$).

$CuSO_4 \cdot 5H_2O$

Basing on thermodynamic additivities of compound formation from element constants (K_f):

$$\log K = \sum v_i \log K_{f, \ i} \tag{14}$$

on Barin's tables [24] and on Eq. (5) the following relation has been fixed for reaction (12):

$$\ln \alpha_{eq} = 17.81 - 6667/T, \qquad 250 \ K \leq T \leq 450 \ K$$

$$T_{eq} = 374.3 \ K, \qquad \Delta H = 110.9 \ kJ \ mol^{-1} \tag{15}$$

The curves α *vs.* T obtained experimentally for 5 heating rates (q) have been presented on the background of relation (15) (Fig. 1). Coefficients of Eq. (1) depend non-linearly on heating rates (Fig. 2) and correlations in linear relations (6) and (7) are extremely important (Fig. 3).

As we mentioned earlier, free expressions ($a_2 = 0$) deviate significantly from thermodynamically defined values according to Eq. (5), in spite of very good linear correlation. In result the reaction (10) containing only one coefficient dependent on heating rate has been obtained:

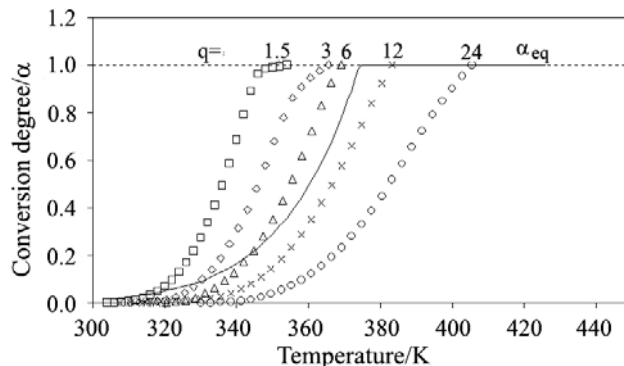$$\alpha = \alpha_{eq} \exp[-a_2 f(T)], \qquad f(T) = \frac{340.83}{T} + \ln T - 6.8334 \tag{16}$$

Fig. 1 Relation between conversion degree and temperature for 5 heating rates:
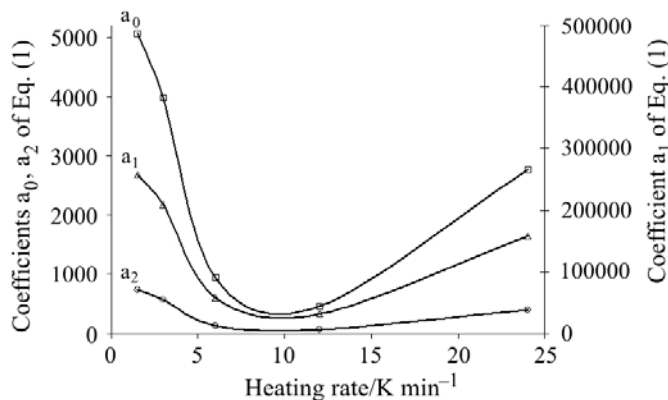q=1.5–3–6–12–24 K min^{-1} on the background of equilibrium line for reaction (12)

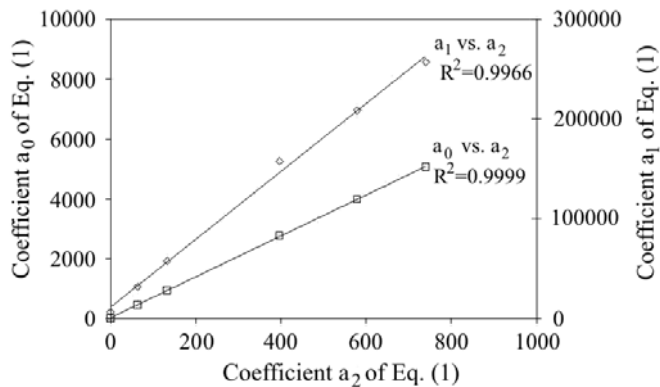**Fig. 2** Relation between coefficients of formula (1) and heating rate for reaction (12)

Fig. 3 Linear relations (6) and (7) for reaction (12): a_0=31.262+6.8334a_2,
$\Delta H/vRT_{eq}$=r_{eq}/T_{eq}=17.81; a_1=11616+340.83a_2, $\Delta H/vR$=r_{eq}=6667 K
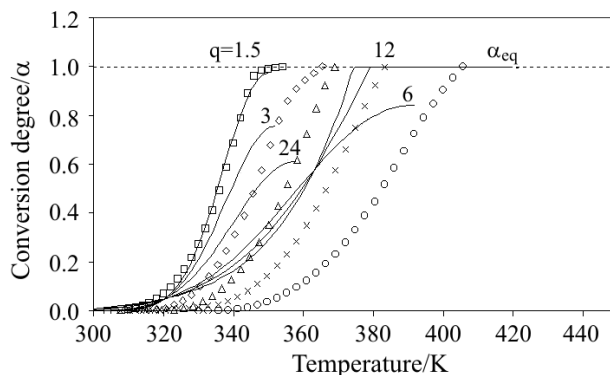
Fig. 4 Relation presented on Fig. 1 with consideration to model (16) for 5 heating rates
(q in K min^{-1}) for reaction (12)

Thus, Fig. 4 is the first interpretation of Eq. (10) and relation illustrated by Fig. 1.

Already superficial analysis of Fig. 4 shows that relation (16) may make us satisfied only partially. It is necessary to remark that this relation has been created by estimation of coefficients of Eq. (1) and by linear relations (6) and (7) fixed between these coefficients, so by three coefficients finally. One may approach the problem in other way for the purpose of control and rewrite Eq. (16) in form:

$$\ln\eta = a_2\gamma - a_2 T_r/T - a_2\ln T, \qquad q = \mathrm{idem} \qquad (17)$$

and determine the coefficients a_2, γ and T_r for each measure set separately. Figure 5 shows the result which corresponds to successive interpretations of Eq. (10).

Figure 5 much more profitably approach to the aim of investigations, which show strong connection of three-parametric Eq. (1), with regards to thermodynamic equilibrium line (5) and deviations from her, in comparison with Fig. 4.
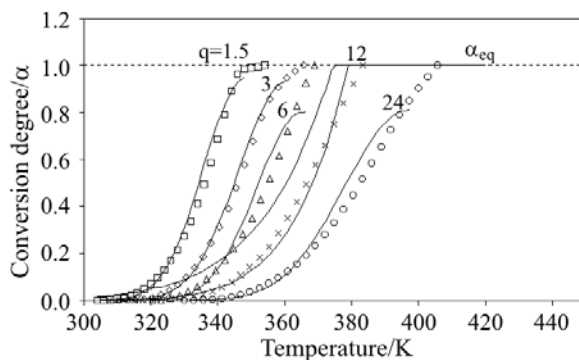

Fig. 5 Relation presented on Figs 1 and 4 with consideration to model (17) for 5 heating rates (q in K min^{-1}) for reaction (12)

PhN(CH$_3$)$_2$·HCl

Equilibrium line for reaction (13) has been taken from [20]:

$$\ln\alpha_{eq}=20.798-8704.3/T, \qquad 0.1\le\alpha_{eq}\le0.74$$

$$T_{eq}=418.6 \text{ K}, \qquad\qquad \Delta H=145 \text{ kJ mol}^{-1}$$

(18)

The relation presented on Fig. 6 has been obtained by carrying the formula (17) as correct and taking different coefficients for changeable heating rates. In this case for 5 experimental curves $f(T)>0$ what makes easier their interpretation.
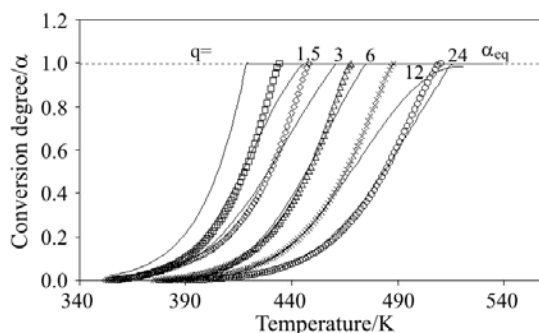

Fig. 6 Relation between conversion degree and temperature on the background of equilibrium line (q in K min^{-1}) for reaction (13)

Thus, we observe that experimental curves course below the curve of equilibrium conversion degree. The coefficient a_2 show domination of temperature function $f(T)$, although a_2 values are not so large ($a_2=95.7-170.4$). In relation to [20] it was impossible to obtain synthesized amine hydrochloride in form of compound of which melting point would be conformable with [23]. It may explain impeded decomposition with regard to necessity of moisture evaporation, because the preparation has been strongly hygroscopic.

Discussion

The trial of presentation of three-parametric Eq. (1) in form (10) containing equilibrium line or, directly, thermodynamic yield of reaction (11) points to very substantial meaning of factor $-a_2f(T)$ in interpretation of relation α *vs. T* in dynamic conditions. The discussed factor is of kinetic nature and it is a measure of distance from equilibrium state and, at the same time, of conventional reaction rate, or of relative rate of reaction of thermal decomposition according to Eq. (2).

Nevertheless we may remark some causes, when $f(T)>0$ (Fig. 6). Then we observe $\alpha<\alpha_{eq}$, conformable to the expectation. But deviation from equilibrium line may also appear on the left, because product $-a_2f(T)$ will be positive (when $f(T)<0$) and increase of experimental conversion degree will take place.

This result may be explained by Le Chatelier's theory [13], or by inequality $\Delta V \mathrm{d}p/\mathrm{d} < 0$, which for standard volume of stoichiometric reaction $\Delta V° > 0$ (gaseous products are formed) imply $\alpha > \alpha_{eq}$ and quantitative connection is given by van Laar and Planck's isotherm:

$$\left(\frac{\partial \ln K}{\partial p} \right)_{\mathrm{T}} = -\frac{\Delta V°}{RT} \tag{19}$$

Using formula (4) and $\Delta V° = vRT / p$ we obtain for $p > 0$ and $p° \cong 0.1 \mathrm{MPa}$:

$$\alpha = \alpha_{eq} (p°/p), \ T = \mathrm{idem} \ \text{for} \ p° > p \geq \alpha_{eq} p° \ \text{and} \ 0 < \alpha_{eq} < 1 \tag{20}$$

In this case α is equilibrium conversion degree with regard to decreased pressure (p) in relation to atmospheric pressure $p°$. Quantitative profiting from formula (20) requires knowledge about value of this pressure, what makes difficult quantitative estimate of the phenomenon.

With regard to conditions of leading the endothermic process of thermal decomposition, it means that changing heating rate and intensity of flow of inert gas, then $\alpha > \alpha_{eq}$. The results of thermal decomposition of $CaCO_3$ [1, 4, 5], which occur for this condition, may be an example. Thus, one may carry that thermodynamic state $\mathrm{d}p < 0$, which is often neglected and introduced during investigations, determines relation (5). In addition, in case of water elimination in low temperatures, one may observe the phenomenon of liquid thermodesorption [25], which demonstrates facilitated course of its evacuation into gas phase at low values of heating rates.

Conclusions

- Thermodynamic interpretation of three-parametric equation has been proposed by introducing equilibrium line. One proved that this equation contains as well thermodynamic part (α_{eq}) as kinetic one in form of coefficient a_2 and temperature function $f(T)$ product.
- The ideal course of thermal decomposition according to Eq. (5) in whole range of α changeability is rarity in dynamic conditions. Formally, this equation presents linear function $\ln\alpha_{eq}$ *vs.* $1/T$ and then straight-line slope is presented by $(-\Delta H/vR)$. With regard to unavoidable measure errors ($\alpha_{eq} \rightarrow \alpha$), the straight-line $\ln\alpha$ *vs.* $1/T$ may also signify thermokinetic relation with slope $(-E/R)$ for 0th and n^{th} order reaction/processes.
- The frequently observed inequalities $\alpha > \alpha_{eq}$ happen, when one do not take into consideration changeable pressure conditions ($\mathrm{d}p < 0$), which set new equilibrium lines in relation to α_{eq} *vs.* T for $p = \mathrm{const.}$ out of heating rate and flow of inert gas.
- By treating our consideration widely, we may be tempted to say a thesis that dynamic conditions ($q > 0$) interlace kinetic and thermodynamic considerations mutually, what is the reason of unsynonymy, because one create excessive interpretation possibilities.

Symbols

a_1, a_2, a_3	coefficients of three-parametric equation, acc. to Eq. (1)
α	conversion degree, $0 \leq \alpha \leq 1$
E	activation energy/J mol^{-1}
$f(T)$	temperature function
γ	slope in Eq. (6)
ΔH	enthalpy/J mol^{-1}
η	thermodynamic yield, $0 \leq \eta \leq 1$
K	thermodynamic equilibrium constant
v	stoichiometric coefficient
p	pressure/Pa
q	heating rate/K min^{-1}
r	relative rate of reaction of thermal decomposition/K
R	8.314 J mol^{-1} K^{-1}
R^2	determination coefficient, $0 \leq R^2 \leq 1$
t_m	melting point/ºC
T	temperature/K
T_r	slope in Eq. (7)/K
ΔV	volume of stoichiometric reaction/m^3

Subscripts:

eq	equilibrium state
i	number of chemical compound
f	formation

Superscripts:

o	standard conditions
(s), (g)	solid and gaseous state, respectively

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