Journal of Thermal Analysis, Vol. 38 (1992) 37-49

NON-ISOTHERMAL KINETICS–CURRENT PROBLEMS

E. Segal

DEPARTMENT OF PHYSICAL CHEMISTRY, FACULTY OF CHEMISTRY, UNIVERSITY OF BUCHAREST, BULEVARDUL REPUBLICII 13, BUCHAREST, ROMANIA

The author presents some experimental and theoretical contributions in non-isothermal kinetics developed in the last years. Special emphasis is given on heterogeneous kinetics with the help of Q-derivatograph, kinetic indexes of thermal stability and on the classical non-isothermal change (CNC).

Keywords: heterogeneous kinetics, non-isothermal kinetics

Introduction

I shall begin with some kinetic applications of the results obtained by means of Q-derivatograph. In a recent reference work concerning the physico-chemical applications of the Q-derivatograph Logvinenko *et al.* [1] mainly dealt with thermodynamically controlled reactions which occur in the so-called quasi-equilibrium conditions. The authors open a window for the kinetic application of the Q-derivatograph. Some of our contributions prior to the appearance of the above mentioned work are, in our opinion exactly in the spirit of such a message.That is the reason I want to begin with such a topic. As known for a heterogeneous decomposition of the form:

$$A_{(s)} \rightarrow B_{(s)} + C_{(g)} \tag{I}$$

the reaction rate is given by:

$$\frac{d\alpha}{dt} = A\, e^{-\frac{E}{RT}} f(\alpha) \tag{1}$$

where α is the degree of conversion, t – the time, A –the preexponential factor, E – the activation energy, R – the gas constant and T – the temperature (K).

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

The function $f(\alpha)$ usually called conversion function depends on the particular reaction mechanism. In common non-isothermal kinetics the variable t from the left side of Eq. (1) is eliminated by using linear [2] hyperbolic [3] and parabolic [4] heating programmes. The use of the Q-derivatograph allows us to suggest another way to eliminate t, namely by recording TG curves in isokinetic conditions [5].

$$\frac{d\alpha}{dt} = C \tag{2}$$

where C is a constant. Through integration, taking into account that $\alpha = 0$ for $t = 0$, Eq. (2) leads to

$$\alpha = Ct \tag{3}$$

In order to fulfil the condition (2) as α and $f(\alpha)$ change in time, the experimental device has to provide for such temperature changes which keep the validity of the relationship:

$$Ae^{-\frac{E}{RT}} = \frac{C}{f(\alpha)} \tag{4}$$

Using Eq. (4) in the form:

$$\ln A - \frac{E}{RT} + \ln f(\alpha) = \ln C \tag{5}$$

and the following general form of the conversion function [6]:

$$f(\alpha) = \alpha^m (1 - \alpha)^n \tag{6}$$

we suggest to characterize the sensitivity of the isokinetic curves to the changes in the reaction rate and kinetic parameters by using the following quantities

$$D_C = \left(\frac{dT}{d\ln C}\right)_{\alpha=\alpha_i} = \frac{E}{RG_i^2} = \frac{R}{E} \cdot T_i^2 \tag{7}$$

$$D_E = \left(\frac{dT}{dE}\right)_{\alpha=\alpha_i} = \frac{1}{RG_i} = \frac{T_i}{E} \tag{8}$$

$$D_A = \left(\frac{\mathrm{d}T}{\mathrm{d}\ln A}\right)_{\alpha=\alpha_i} = -\frac{RT_i^2}{E} \tag{9}$$

$$D_m = \left(\frac{\mathrm{d}T}{\mathrm{d}m}\right)_{\alpha=\alpha_i} = -\frac{RT_i^2}{E}\cdot\ln\alpha_i \tag{10}$$

$$D_n = \left(\frac{\mathrm{d}T}{\mathrm{d}n}\right)_{\alpha=\alpha_i} = -\frac{RT_i^2}{E}\cdot\ln(1-\alpha_i) \tag{11}$$

where

$$G_i = \ln A + \ln f(\alpha_i) - \ln C_i \tag{12}$$

or taking into account (5)

$$G_i = \frac{E}{RT_i} \tag{13}$$

For a solid-gas decomposition of the form (I) with the following kinetic and operational parameters.

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = 1.7\cdot 10^{-5}\ \mathrm{s}^{-1}$$

$$\alpha_i = \tfrac{1}{2}$$

$A = 6.23 \cdot 10^6\ \mathrm{s}^{-1}$, $E = 20$ kcal·mole $^{-1}$, $m = 1$, $n = 0$ or $m = 0$, $n = 1$
one obtains:

$$D_G = 15\ \mathrm{K},\ D_E = 19.5\ \mathrm{mole\cdot K\cdot kcal^{-1}},\ D_A = -15\ \mathrm{K}$$

$$D_m = D_n = 10.4\ \mathrm{K}$$

Thus a 2.7 times increase in the reaction rate increases the temperature corresponding to the half conversion point of the isokinetic curve by 15 K. The temperature interval (separation), D_E, between two isokinetic curves for two decomposition reactions which differ only by the activation energy values is 19.5 K when E_2–E_1 = 1 kcal·mol^{-1}. As $D_A < 0$ and $D_E > 0$, it follows that the increase of the preexponential factor has an opposite effect to the increase of the activation energy. Consequently, the simultaneous increase of the parameters E and A could mutually compensate, leaving the position of the isokinetic curve unchanged (compensation effect). Changes by one unit of the parameters m and n shift the isokinetic curve by 10.4 K.

Equation (10) shows that the parameter, m, influences the initial accelerating period of the isokinetic curve where $\alpha<1$, but does not influence the final period ($D_m \rightarrow 0$ for $\alpha \rightarrow 1$).

On the contrary, according to Eq. (11) the n parameter influences the final (decelerating period) as $D_n \rightarrow 0$ for $\alpha \rightarrow 0$. The isokinetic curves in Fig. 1 illustrate these last statements and show that for $m \neq 0$ and $n \neq 0$ the curves $T(\alpha)$ exhibit a minimum.

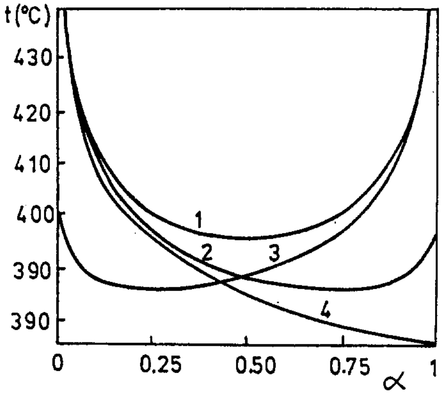

Fig. 1a The influence of the kinetic parameters m and n on the position and shape of the isokinetic curves
a) $n_1 = 0$, $n_2 = 1/3$, $n_3 = 1/2$, $n_4 = 2/3$, $n_5 = 1$, $n_6 = 2$, $m_{1\text{-}6} = 0$, $E_{1\text{-}6} = 20$ kcal·mole^{-1}, $A_{1\text{-}6} = 6.23\cdot 10^6$ s^{-1}, $C_{1\text{-}6} = 1/6\cdot 10^{-4}$ s^{-1}

From Eq. (5) taking the first derivative of temperature with respect to α one obtains

$$\frac{\mathrm{d}T}{\mathrm{d}\alpha} = -\frac{RT^2}{E}\cdot\frac{\mathrm{d}\ln f(\alpha)}{\mathrm{d}\alpha} \tag{14}$$

Equation (14) for $f(\alpha)$ given by (6) takes the form:

$$\frac{\mathrm{d}T}{\mathrm{d}\alpha} = \frac{RT^2}{E}\cdot\frac{\alpha(m+n)-m}{\alpha(1-\alpha)} \tag{15}$$

The condition for the minimum of the curve T *vs.* $\alpha\cdot\left(\frac{\mathrm{d}T}{\mathrm{d}\alpha}\right)_{\min}=0$ leads to:

$$\frac{\alpha_{\min}}{1-\alpha_{\min}} = \frac{m}{n} \tag{16}$$

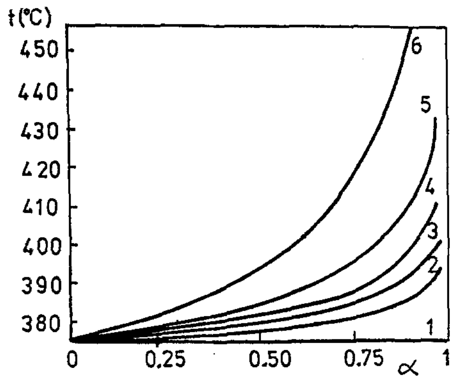

Fig. 1b The influence of the kinetic parameters m and n on the position and shape of the isokinetic curves
b) $m_1 = n_1 = 1$, $m_2 = 1$, $n_2 = 1/3$, $m_3 = 1/3$, $n_3 = 1$, $m_4 = 1$, $n_4 = 0$, $E_{1-4} =$ 20 kcal·mole^{-1}, $A_{1-4} = 6.23\cdot10^6$ s^{-1}, $C_{1-4} = 1/6\cdot10^{-4}$ s^{-1}

Taking into account all these results one can outline the way to evaluate the kinetic parameters in isokinetic conditions. A family of isokinetic curves corresponding to the constant reaction rates (C_1, C_2...) for various heating rates should be recorded.

Then the temperatures (T_1, T_2 ...) corresponding to the same value of degree of conversion (as for example $\alpha = \frac{1}{2}$) should be considered. For the chosen isoconversion condition the term $\ln f(\alpha)$ in Eq. (5) is constant thus the plot of $\ln C$ *vs.* the reciprocal values of the temperature should be a straight line. From the slope of this straight line $-\frac{\Delta \ln C}{\Delta\left(\frac{1}{T}\right)}$ the activation energy can be calculated according to the relationship:

$$E = -R\cdot\frac{\Delta \ln C}{\Delta\left(\frac{1}{T}\right)} \tag{17}$$

For other isoconversion conditions ($\alpha = 1/4$, $\alpha = 3/4$, etc.) the same value of the activation energy should be obtained. If the condition is not fulfilled, it means that the reaction mechanism changes with the degree of conversion. As it was previously shown, if the isokinetic curve exhibits a minimum , it means that $m \neq 0$ and $n \neq 0$. To obtain the values of these parameters one has to consider the characteristic points of the isokinetic curve (Fig. 2) where $\alpha_C = 1/4$, $\alpha_D = \alpha_{\min}$ and $\alpha_I = 3/4$. According to (5) for $\alpha_1 = 1/4$ and $\alpha_2 = 3/4$, it turns out that

$$\frac{\left(\frac{\mathrm{d}T}{\mathrm{d}\alpha}\right)_{1/4}}{\left(\frac{\mathrm{d}T}{\mathrm{d}\alpha}\right)_{3/4}} = \frac{(3m-n)T_{1/4}^{2}}{(m-3n)T_{3/4}^{2}} \tag{18}$$

The evaluation of the parameters m and n can be considerably simplified if Eqs (16) and (18) are transcribed in terms of moduli of some segments of straight line which could be measured in arbitrary units (such as *cm*) on the curve recorded by the experimental device. Figure 2 shows that

$$\frac{m}{n} = \frac{\overline{JK}}{\overline{KL}} \tag{19}$$

$$\frac{(3m-n)T_{1/4}^{2}}{(3n-m)T_{3/4}^{2}} = \frac{\overline{FH}}{\overline{AF}} \tag{20}$$

For every pair of points B and G which fulfil the condition $T_\mathrm{B} = T_\mathrm{G}$ taking into account Eq. (5) and relationship (6), one finds that

$$\frac{m}{n} = \frac{\ln\frac{1-\alpha_\mathrm{B}}{1-\alpha_\mathrm{G}}}{\ln\frac{\alpha_\mathrm{G}}{\alpha_\mathrm{B}}} \tag{21}$$

or according to Fig. 2:

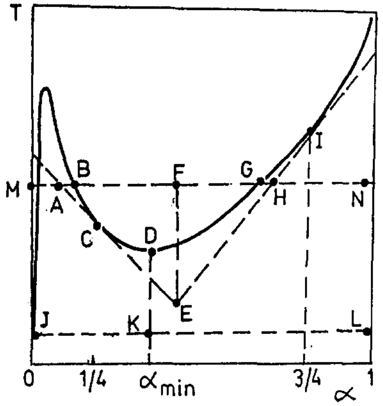

Fig. 2 The relationships between the shape of the kinetic curve and the parameters of conversion functions (6) (see relationships (19)–(23))

$$\frac{m}{n}=\frac{\ln\frac{\overline{BN}}{\overline{GN}}}{\ln\frac{\overline{MG}}{\overline{MB}}} \tag{22}$$

The last relationship is useful for checking the constancy of the ratio $\frac{m}{n}$ for the entire extent of the isokinetic curve. For symmetrical curves $\overline{JK}=\overline{KL}$, $m=n$ and $\alpha_{\min}=\frac{1}{2}$.

The curves T *vs.* α which do not exhibit a minimum ($\alpha_{\min}\rightarrow 0$) and are characterized by a positive slope $\left(\frac{\mathrm{d}T}{\mathrm{d}\alpha}>0\right)$, are described by a conversion function of the form:

$$f(\alpha)=(1-\alpha)^n \tag{23}$$

For this case ($m=0$) Eq. (15) becomes:

$$\frac{\mathrm{d}T}{\mathrm{d}\alpha}=\frac{RT^2}{E}\cdot\frac{n}{1-\alpha} \tag{24}$$

The parameter n can be estimated from Eq. (24) using the measured slope of the isokinetic curve for a given value of the degree of conversion. As an example for $\alpha=1/2$, Eq. (24) leads to:

$$n=\frac{E}{2RT^2_{1/2}}\cdot\left(\frac{\mathrm{d}T}{\mathrm{d}\alpha}\right)_{1/2} \tag{25}$$

The lack of a minimum on the curve T *vs.* α ($\alpha_{\min}=1$) together with a negative slope of the isokinetic curve $\left(\frac{\mathrm{d}T}{\mathrm{d}\alpha}<0\right)$ means that $n=0$ and the decomposition is described by:

$$f(\alpha)=\alpha^m \tag{26}$$

In this case the particular form of Eq. (15) is

$$\frac{\mathrm{d}T}{\mathrm{d}\alpha}=-\frac{RT^2}{E\alpha}\cdot m \tag{27}$$

For $\alpha=1/2$, the parameter m can be calculated with the help of the formula:

$$m = -\frac{E}{2RT_{1/2}^2}\cdot\left(\frac{\mathrm{d}T}{\mathrm{d}\alpha}\right)_{1/2} \tag{28}$$

Once E, m and n are known, the preexponential factor can be calculated using Eq. (5).

As it was previously shown, the Q-derivatograph meets the requirements of an isokinetic curve to a certain extent [1–9]. The experimental isokinetic curve for the dehydration of calcium oxalate is given in Fig. 3.

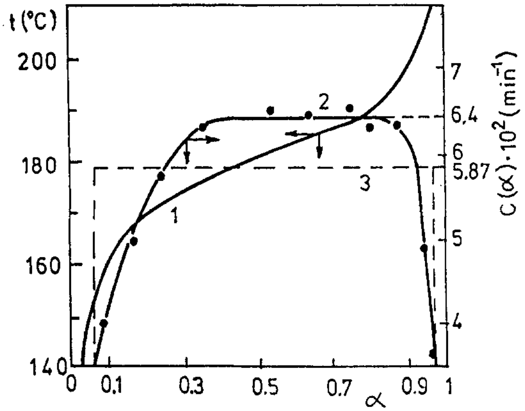

Fig. 3 The experimental isokinetic curve for the dehydration of $CaC_2O_4 \cdot H_2O$. 2. The curve $C(\alpha)$, 3. The plot of C *vs.* degree of conversion

The curve has been recorded using the following operational conditions : sample weight $m = 0.1059$ g, applied reaction rate $\mathrm{d}m/\mathrm{d}t = 0.2\ \mathrm{mg\cdot min^{-1}}$, heating rate until the isokinetic region $\frac{\mathrm{d}T}{\mathrm{d}t} = 3\ \mathrm{deg\cdot min^{-1}}$, initial voltage $U_o = 75$ V, quasiflat platinum crucible of weight $m_c = 0.740$ g, temperature scale 250°.

To check the extent of the fulfilment of the isokinetic condition, the curve $C(\alpha)$ (curve 2) has been given in the same Fig. The mean value $\overline{C}_\alpha$ of the dehydration rate with respect to α (curve 3) is given, too. The dehydration rate was determined from the α *vs.* T curve which was recorded through points, two successive points being separated by time interval $\Delta t = 0.1$ min. In order to calculate the mean value of the dehydration rate we used the formula:

$$\overline{C} = \frac{1}{\alpha_2 - \alpha_1}\cdot\int_{\alpha_1}^{\alpha_2} C(\alpha)\,\mathrm{d}\alpha \tag{29}$$

in which the integration was performed graphically for $0.04 \le \alpha \le 0.98$. It should be noticed that the rate is constant only for $0.4 \le \alpha \le 0.9$. Actually, the experimental curve consists of three regions, namely

I. $0.04 \le \alpha \le 0.4$; region of linear heating;

$$\frac{dT}{dt} = 3 \text{ deg}\cdot\text{min}^{-1},\ 0 \le \frac{d\alpha}{dt} \le 6.4\cdot 10^{-2} \text{ min}^{-1}$$

II. $0.4 \le \alpha \le 0.9$; isokinetic region with variable heating rate;

$$0 \le \frac{dT}{dt} \le 3 \text{ K}\cdot\text{min}^{-1};\ \frac{d\alpha}{dt} = 6.4\cdot 10^{-2} \text{ min}^{-1}$$

III. $0.9 \le \alpha \le 1$; region of linear heating;

$$0 \le \frac{d\alpha}{dt} \le 6.4\cdot 10^{-2} \text{ min}^{-1};\ \frac{dT}{dt} = 3 \text{ deg}\cdot\text{min}^{-1};$$

The three above mentioned regions can be approximated using one quasi-isokinetic theoretical curve which corresponds to a constant decomposition rate for the whole time interval.

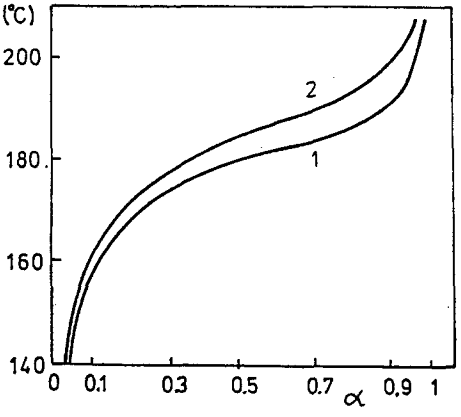

Fig. 4 The change of the shape and position of the experimental quasi-isokinetic curves with the decomposition rate for dehydration of $Ca(C_2O_4)_2 \cdot H_2O$ 1. $C = 5.9\cdot 10^{-2}\text{min}^{-1}$; 2. $C = 8.6\cdot 10^{-2}\text{min}^{-1}$

To estimate the kinetic parameters, it is necessary to record at least two isokinetic curves. Such curves for calciumoxalate dehydration are given in Fig. 4. The corresponding values of half the conversion temperature are, respectively; $t = 180°$ and $t = 186°$.

The decomposition rate cannot be changed in large limits to get a family of isokinetic curves due to the inertia of the thermoregulator as well as to the mass and heat transfer phenomena which give rise to deformations of the experimental curves.

As the experimental curves α *vs.* T do not exhibit a minimum and their slope is positive it follows that $m = 0$ and $f(\alpha) = (1-\alpha)^n$. The processing of the experimental data from the middle region of the isokinetic curves using relationships (5), (17) and (25) leads to the following values of the kinetic parameters, which are compared with those obtained by using other methods.

Isokinetic method	Hyperbolic heating method [3]	DTA method [10]
$n = 1.15$	$n = 1$	$n = 1$
$E = 26\ \text{kcal}\cdot\text{mole}^{-1}$	$E = 23.5\ \text{kcal}\cdot\text{mole}^{-1}$	$E = 21.8\ \text{kcal}\cdot\text{mole}^{-1}$
$A = 7.5\cdot 10^9\ \text{s}^{-1}$	$A = 8\cdot 10^6\ \text{s}^{-1}$	$A = 6.23\cdot 10^6\ \text{s}^{-1}$

The inspection of these results show that the isokinetic method leads to slightly higher values of the kinetic parameters. It is interesting to notice that for a sample with a rather high weight ($m = 300$ mg) in the usual crucible for derivatograph, the partial pressure of water being more close to the atmospheric pressure, the experimental value obtained for the activation energy is $E = 97$ kcal/mol. Due to the fact that the dehydration rate is constant and the conversion function at the half conversion point cannot vary in large limits it turns out that according to Eq. (4) the increase of the activation energy is going to be compensated mainly by the increase of the preexponential factor ($A = 2.8\cdot 10^{38}\ \text{s}^{-1}$) and to a smaller extent by the decrease of n ($n = 0.2$). When using a labyrinth type crucible a trend to zero in the slope of the T *vs.* α curves has been noticed and their position is not influenced by the reaction rate value any more. From a kinetic standpoint according to relationship (24) in such conditions the value of a E and n are as followes $E \to \infty$ and $n \to 0$.

The increase of the apparent activation energy values with the partial pressure of the volatile component reported long time ago for the isothermal decomposition of some carbonates is known as the Zawadski–Bretszneider effect [11, 12].

A sample of $KMnO_4$ with $m = 0.2194$ g was submitted to decomposition in the same operating conditions. The only difference was that a covered crucible (to avoid weight losses due to decrepancies of $KMnO_4$ crystal) was used. The curve t° *vs.* α is given in Fig. 5.

The minimum point exhibited by the curve t° *vs.* α indicates the autocatalytic character of the reaction, its kinetic is described by Eq. (6) with

$m \neq 0$ and $n \neq 0$ in agreement with literature data for the isothermal decomposition [13–15].

The curve given in Fig. 5 is distorted due to the inertia of the thermoregulator as well as the mass and heat transfer phenomena so that the condition $\frac{d\alpha}{dt} = C$ is fulfilled only in a narrow range of conversion ($0.42 \leq \alpha \leq 0.69$). In such conditions the kinetic parameters cannot be determined and we have to be satisfied only with a qualitative result.

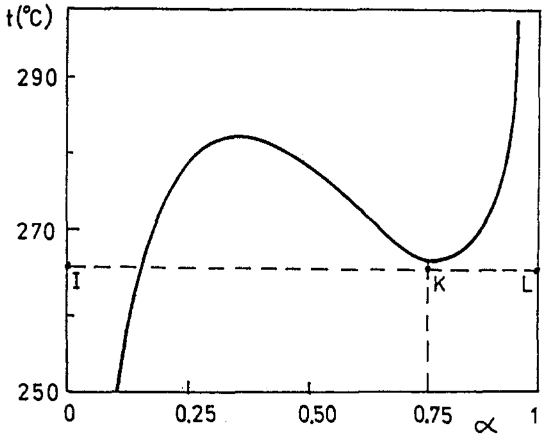

Fig. 5 The quasiisokinetic experimental curve for the decomposition of KMnO4

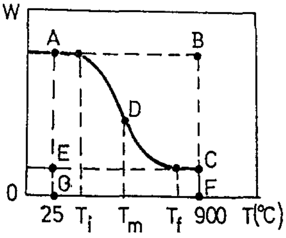

Fig. 6 The characteristic temperatures of the TG curves and the areas necessary to evaluate the correct temperature index (W – weight of the sample, T – temperature)

As a conclusion concerning the isokinetic curves method one has to say that it is a promising method mainly for the possibilities to establish the form of the conversion function from its shape and to evaluate the activation energy no matter the analytical form of the conversion function.

Table 1 Kinetic parameters and kinetic thermal stability indexes values (β = 10 K(min))

Material	Step	E, kcal·mole^{-1}	n	A, s^{-1}	Temperature interval, °C	$k(T_i)$, s^{-1}	$I_k = \frac{1}{k(T_i)}$	$\log I_k$	r*
1. Bakelite	1	24.6	1	$4.5\cdot10^{6}$	160 – 380	$2.1\cdot10^{-6}$	$4.5\cdot10^{5}$	5.7	0.999
	2	15.6	1	38	380 – 610	$2.4\cdot10^{-4}$	$4.1\cdot10^{3}$	3.6	0.990
2. Polyethylene	1	15.9	1	$1.8\cdot10^{3}$	230 – 380	$2.5\cdot10^{-4}$	$4.0\cdot10^{3}$	3.6	0.992
	2	29.1	1	$2.6\cdot10^{6}$	380 – 550	$5.5\cdot10^{-4}$	$1.8\cdot10^{3}$	3.2	0.994
3. Insulation rubber	1	22.4	1	$6.8\cdot10^{5}$	230 – 380	$1.5\cdot10^{-4}$	$6.9\cdot10^{3}$	3.8	0.990
	2	36.6	1	$5.7\cdot10^{8}$	380 – 470	$3.8\cdot10^{-4}$	$2.6\cdot10^{3}$	3.4	0.994
4.ABS	1	20.0	1	$2.5\cdot10^{3}$	250 – 470	$1.3\cdot10^{-5}$	$7.9\cdot10^{4}$	4.9	0.988
	2	40.6	0	$1.0\cdot10^{8}$	470 – 630	$1.4\cdot10^{-4}$	$7.2\cdot10^{3}$	3.9	0.950
5. Polyamide (Relon)	1	26.4	1	$1.9\cdot10^{5}$	290 – 520	$1.2\cdot10^{-5}$	$8.2\cdot10^{4}$	4.1	0.985
	2	–	–	–	520 – 610	–	–	–	–
6. Polycarbonate	1	36.2	1	$2.8\cdot10^{8}$	330 – 510	$4.6\cdot10^{-5}$	$3.8\cdot10^{4}$	4.6	0.992
	2	21.6	1	$3.8\cdot10^{8}$	510 – 620	$3.9\cdot10^{-3}$	$2.5\cdot10^{2}$	2.5	0.969

* r is the correlation coefficient of the linear regression used to evaluate the non-isothermal kinetic parameters

Another topic discussed in the lecture is that of kinetic thermal stability indexes [16]. Special emphasis is given on the temperature corresponding to the beginning of the reaction, T_i, to a corrected temperature , T_c, quite insensitive to the change of the heating rate and to the reciprocal value of the rate constant, $k(T_i)$ (see Table 1).

The final question discussed in the lecture is a theoretical one, dedicated to the isothermal kinetic equations which admit a classical nonisothermal change (CNC). Such equations have been called primary. Some nonisothermal kinetic equations obtained through CNC of primary equations are also analysed. The details concerning such problems are given in the references [17–21].

References

1 V. A. Logvinenko, F. Paulik and J. Paulik, 'Neravnovesnaia termogravimetria v sovremenoi neorganiceskoi himii', Nauka, Novosibirsk 1989.
2 J. H. Flynn and L. A. Wall, J. Res. Nat. Bur. Stand., 70A (1966) 487.
3 G. Ehrlich, Adv. Catal., 14 (1963) 255; J. Zsakó, J. Thermal Anal., 2 (1970) 141; J. Simon and E. Debreczeny, J. Thermal Anal., 3 (1977) 301; D. Fatu and E. Segal, Rev. Roum. Chim., 16 (1971) 343.
4 E. Segal and V. Marcu, Thermochim. Acta, 24 (1978) 178.
5 D. Fatu and E. Segal, Thermochim. Acta, 61 (1983) 215.
6 J. Šestak, Thermophysical Properties of Solids, Academia, Prague 1984, p. 223.
7 F. Paulik and J. Paulik, Anal. Chim. Acta, 60 (1972) 128.
8 F. Paulik and J. Paulik, Proc. 3rd int. Conf. Thermal Anal. Davos, Vol. 1, 1972, p. 161.
9 F. Paulik and J. Paulik, Hung. Sci. Instr., 38 (1976) 17.
10 D. Fatu, J. Thermal Anal., 1 (1969) 285.
11 J. Zawadski and S. Bretszneider, Z. Elektrochem., 41 (1935) 215.
12 M. M. Pavliucenko and E. A. Prodan, Dokl. Akad. Nauk, SSSR, 136 (1961) 651.
13 P. W. M. Jacobs and F. C. Tompkins, in W. E. Garner, 'Chemistry of the Solid State' Butterworths, London 1955, p. 197.
14 M. S. Z. Roghinski, Ghetero. Katal., Nauka, Moscow 1979, p. 180.
15 D. Fatu, Rev. Roum. Chim., 23 (1978) 1029.
16 D. Fatu, G. Geambas, E. Segal, P. Budrugeac and Sanda Ciutacu, Thermochim. Acta, 149 (1989) 181.
17 E. Urbanovici and E. Segal, Thermochim. Acta, 118 (1987) 335.
18 E. Urbanovici and E. Segal, Thermochim. Acta, 118 (1987) 65.
19 L. D. Landau and E. M. Lifshits, 'Mekhanika', Nauka, Moscow 1965.
20 I. G. Murgulescu, T. Oncescu and E. Segal, 'Introducere in chimia fizica', V.II,2, Academie, Bucuresti 1981.
21 T. Kemeny and J. Šestak, Thermochim. Acta, 110 (1987) 113.

Zusammenfassung — Es werden einige, in den vergangenen Jahren entwickelte experimentelle und theoretische Beiträge zur nichtisothermen Kinetik dargestellt. Besonders betont werden heterogene Kinetik mittels Q-Derivatografie, kinetischer Index der thermischen Stabilität sowie klassische nichtisotherme Umwandlungen (CNC).