Thermochimica Acta, 61 (1983) 215–225
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

ISOKINETIC CONDITIONS FOR VALUATION OF KINETIC PARAMETERS

D. FĂTU and E. SEGAL

Department of Physical Chemistry and Electrochemical Technology, Faculty of Chemical Engineering, Polytechnical Institute of Bucharest, Bucharest (Romania)

(Received 22 July 1982)

ABSTRACT

A method was worked out for the valuation of kinetic parameters from two or more α vs. T curves obtained in isokinetic conditions, i.e. by keeping the reaction rate, $d\alpha/dt$, at a constant value. The method was checked by using some theoretical families of calculated isokinetic curves, as well as by working the experimental data concerning the isokinetic dehydration of $CaC_2O_4 \cdot H_2O$ and the thermal decomposition of $KMnO_4$.

THEORETICAL BACKGROUND

For a heterogeneous decomposition of the type

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

the reaction rate is given by

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

where α = conversion degree, t = time, A = the pre-exponential factor, E = activation energy, R = the gas constant and T = temperature (K). The function f(α) is usually called the conversion function, and depends on the particular reaction mechanism. In common non-isothermal kinetics, the variable t is eliminated by using linear [1], hyperbolic [2] and parabolic [3] heating programmes. In this paper, we suggest another way to eliminate t from the left side of eqn. (1) by recording TG curves in isokinetic conditions, for which

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

where C_i is a constant. Through integration for the initial condition $\alpha = 0$ at $t = 0$, eqn. (2) leads to

$$\alpha = C_i t \tag{3}$$

In order to fulfil the condition in eqn. (2) as α and $f(\alpha)$ change with time, the experimental device has to provide for such temperature changes that maintain the validity of the relationship

$$A\,e^{-E/RT} = \frac{C_i}{f(\alpha)} \tag{4}$$

From the thermogravimetric isokinetic curves α vs. T, $(1-\alpha)$ vs. T or T vs. α, one can get information concerning the reaction kinetics. Indeed, the temperature T_i, corresponding to a given value of $\alpha = \alpha_i$, or the slope $(\mathrm{d}T/\mathrm{d}\alpha)_{\alpha=\alpha_i}$ is related to the kinetic parameters. To illustrate such relationships, we shall start from the following variant of eqn. (4)

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

The derivatives of temperature with respect to $\ln C_i$, E, $\ln A$ and α are

$$D_C = \left(\frac{\mathrm{d}T}{\mathrm{d}\ln C_i}\right)_{\alpha=\alpha_i} = \frac{E}{RG^2} = \frac{R}{E}T^2 \tag{6}$$

$$D_E = \left(\frac{\mathrm{d}T}{\mathrm{d}E}\right)_{\alpha=\alpha_i} = \frac{1}{RG} = \frac{T}{E} \tag{7}$$

$$D_A = \left(\frac{\mathrm{d}T}{\mathrm{d}\ln A}\right)_{\alpha=\alpha_i} = -\frac{RT^2}{E} \tag{8}$$

$$\left(\frac{\mathrm{d}T}{\mathrm{d}\alpha}\right)_{\alpha=\alpha_i} = -\frac{RT^2}{E}\,\frac{\mathrm{d}\ln f(\alpha)}{\mathrm{d}\alpha} \tag{9}$$

where $G > 0$ and

$$G = \ln A + \ln f(\alpha) - \ln C_i \tag{10}$$

A general form of the conversion function for the decomposition of solids is

$$f(\alpha) = \alpha^m(1-\alpha)^n \tag{11}$$

where m and n are constants with different values according to the reaction mechanism. So, the case $m = n = 1$ corresponds to a branching chain nucleation mechanism. From eqns. (1) and (11) with $m = n = 1$, through integration, one gets

$$\ln\frac{\alpha}{1-\alpha} = kt \tag{12}$$

which is known as the Prout and Tompkins equation [4]. For $m = 0$ and $n = 2/3$, eqn. (1), taking into account eqn. (11), leads to

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\,e^{-E/RT}(1-\alpha)^{2/3} \tag{13}$$

which corresponds to the contracting sphere or cube model.

In order to show how parameters m and n influence the position and form of the isokinetic curve, one has to introduce eqn. (11) into eqn. (5) and to perform the derivatives dT/dm and dT/dn. These operations give

$$D_m = \frac{dT}{dm} = -\frac{RT^2}{E} \ln \alpha \tag{14}$$

$$D_n = \frac{dT}{dn} = -\frac{RT^2}{E} \ln(1-\alpha) \tag{15}$$

To characterise the sensitivity of the isokinetic curves to the change in reaction rate and kinetic parameters, we suggest the use of the quantities D_C, D_E, D_A, D_m and D_n defined by eqns. (6), (7), (8), (14) and (15). For a solid–gas decomposition with the following kinetic and operational parameters: $d\alpha/dt = 1.7 \times 10^{-5}\ s^{-1}$, $\alpha_i = \frac{1}{2}$, $A = 6.23 \times 10^6\ s^{-1}$, $E = 20$ kcal mole^{-1}, $m = 1$, $n = 0$, or $n = 1$, $m = 0$ one gets

$D_C = 15$ K, $D_E = 19.5$ mole K kcal^{-1}, $D_A = -15$ K, $D_m = D_n = 10.4$ K

Thus, a 2.7 times increase in the reaction rate increases the half conversion point of the isokinetic curve by 15 K. The temperature interval (separation), D_E, between the isokinetic curves for two decompositions which differ only by the activation energy values, is 19.5 K when $E_2 - E_1 = 1$ kcal mole^{-1}. As $D_A < 0$ and $D_E > 0$ it follows that the increase of the pre-exponential factor has on opposite effect on the increase of 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 in the parameters m and n shift the isokinetic curve 10.4 K. Equations (14) and (15) show that n influences the initial accelerating period of the isokinetic curve where $\alpha < 1$, but does not influence the final period ($D_m \to 0$, $\alpha \to 1$). On the contrary, the change of the m parameter induces changes in the final (decelerating) period. The analysis of the families of isokinetic curves calculated using eqn. (5) and given in Fig. 1, leads to the same conclusions. The relationship between the slope of the curve T vs. α and the m and n parameters can be derived from eqns. (10) and (11). This gives

$$\frac{dT}{d\alpha} = \frac{RT^2}{E} \frac{\alpha(m+n) - m}{\alpha(1-\alpha)} \tag{16}$$

$$\frac{d^2T}{d\alpha^2} = \frac{RT^2}{E\alpha^2(1-\alpha)^2} \left\{ \left[\frac{2RT}{E}(m+n) + 1 \right] (m+n)\alpha^2 - 2m\left[\frac{2RT}{E}(m+n) + 1 \right] \alpha + m\left(\frac{2RTm}{E} + 1 \right) \right\} \tag{17}$$

The condition for the minimum of the curve T vs. α, $(dT/d\alpha)_{\min} = 0$ leads to

$$\frac{m}{n} = \frac{\alpha_{\min}}{1 - \alpha_{\min}} \tag{18}$$

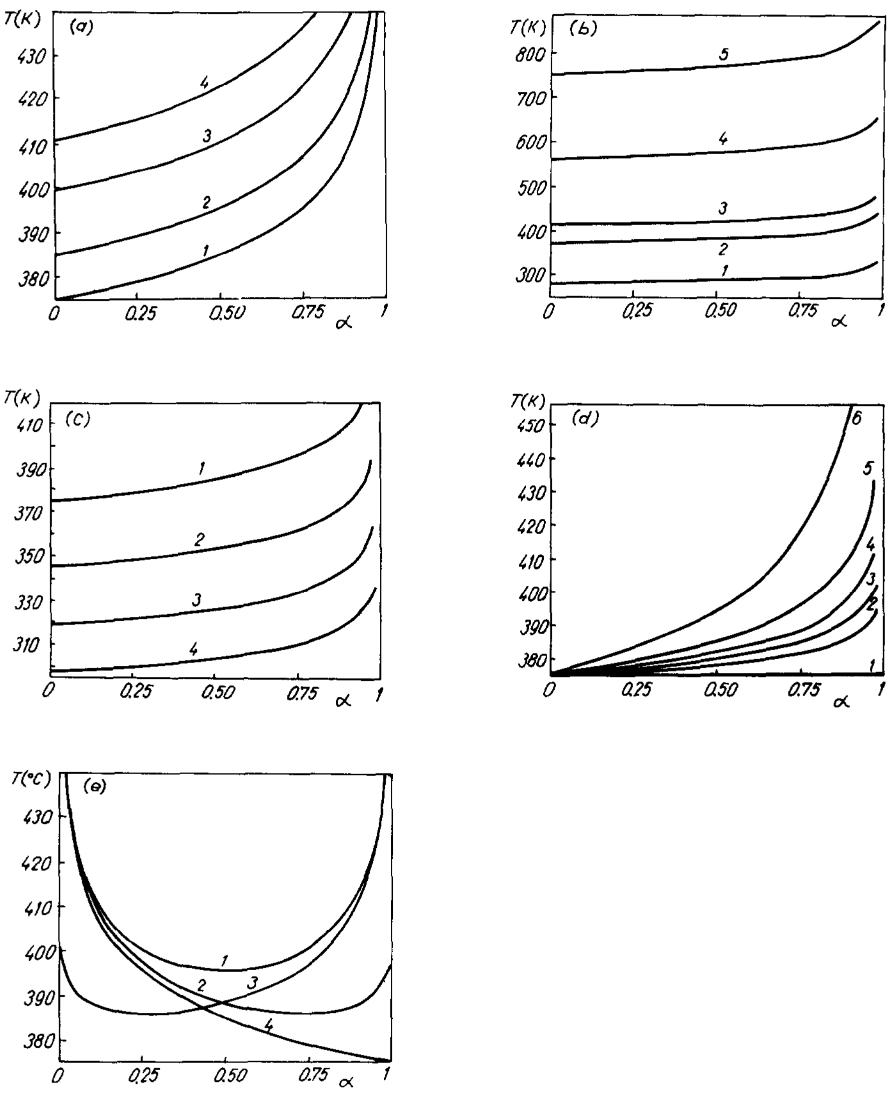

Fig. 1. The influence of the reaction rate and kinetic parameters on the position and shape of the isokinetic curves.

(a) $C_1 = \frac{1}{6} \times 10^{-4}$ s^{-1}; $C_2 = \frac{2}{6} \times 10^{-4}$; $C_3 = \frac{5}{6} \times 10^{-4}$; $C_4 = \frac{10}{6} \times 10^{-4}$: $m_{1-4} = 0$; $n_{1-4} = 1$; $E_{1-4} = 20$ kcal mole^{-1}; $A_{1-4} = 6.23 \times 10^6$ s^{-1}

(b) $E_1 = 15$ kcal mole^{-1}; $E_2 = 20$; $E_3 = 22$; $E_4 = 30$; $E_5 = 40$: $m_{1-5} = 0$; $n_{1-5} = 1$; $A_{1-5} = 6.23 \times 10^6$ s^{-1}; $C_{1-5} = \frac{1}{6} \times 10^{-4}$ s^{-1}

(c) $A_1 = 6.23 \times 10^6$ s^{-1}; $A_2 = 6.23 \times 10^7$; $A_3 = 6.23 \times 10^8$; $A_4 = 6.23 \times 10^9$: $m_{1-4} = 0$; $n_{1-4} = 1$; $E_{1-4} = 20$ kcal mole^{-1}; $C_{1-4} = \frac{1}{6} \times 10^{-4}$ s^{-1}

(d) $n_1 = 0$; $n_2 = \frac{1}{3}$; $n_3 = \frac{1}{2}$; $n_4 = \frac{2}{3}$; $n_5 = 1$; $n_6 = 2$: $m_{1-6} = 0$; $E_{1-6} = 20$ kcal mole^{-1}; $A_{1-6} = 6.23 \times 10^6$ s^{-1}; $C_{1-6} = \frac{1}{6} \times 10^{-4}$ s^{-1}

(e) $m_1 = n_1 = 1$; $m_2 = 1$; $n_2 = \frac{1}{3}$; $m_3 = \frac{1}{3}$; $n_3 = 1$; $m_4 = 1$; $n_4 = 0$: $E_{1-4} = 20$ kcal mole^{-1}; $A_{1-4} = 6.23 \times 10^6$ s^{-1}; $C_{1-4} = \frac{1}{6} \times 10^{-4}$ s^{-1}.

Taking into account eqn. (18), eqn. (5) gives

$$T_{\min}=\frac{E}{R[\ln A+m\ln(m)+n\ln(n)-(m+n)\ln(m+n)-\ln C_i]} \tag{19}$$

Taking into account all these results, one can outline the way to determine the kinetic parameters in isokinetic conditions. A family of isokinetic curves for different heating rates, (C_1, $C_2\ldots$), should be recorded with the help of the experimental device. Then the temperatures, (T_1, $T_2\ldots$), corresponding to the same value of the degree of conversion, as for example for $\alpha=\frac{1}{2}$, should be considered. For the chosen iso-conversion condition, the term $\ln f(\alpha)$ from eqn. (5) is constant, so the plot of $\ln C$ vs. the reciprocal values of the temperature ($1/T$) should be a straight line. The slope of this straight line gives the activation energy using the relationship

$$E=-R\frac{\Delta\ln C}{\Delta(1/T)} \tag{20}$$

For other iso-conversion conditions ($\alpha=\frac{1}{4}$, $\alpha=\frac{3}{4}$, etc.) the same value of the activation energy should be obtained. If the results cannot be linearized in the above mentioned coordinates, it means that the decomposition consists of two or more steps with different values of the activation energy. 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 $\alpha_C=\frac{1}{4}$, $\alpha_D=\alpha_{\min}$ and $\alpha_I=\frac{3}{4}$. When $\alpha_1=\frac{1}{4}$ and $\alpha_2=\frac{3}{4}$, eqn. (16) gives

$$\frac{(\mathrm{d}T/\mathrm{d}\alpha)_{1/4}}{(\mathrm{d}T/\mathrm{d}\alpha)_{3/4}}=\frac{(3m-n)T_{1/4}^2}{(m-3n)T_{3/4}^2} \tag{21}$$

The valuation of the m and n parameters could be considerably simplified if the system of eqns. (18) and (21) was transcribed in terms of the modulus of some segments of straight line which could be measured in arbitrary units

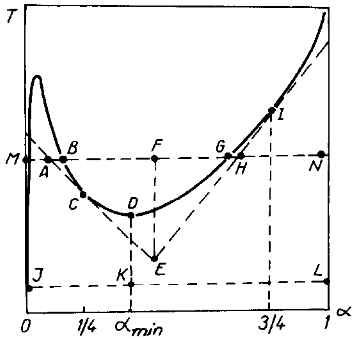

Fig. 2. The relation between the shape of the isokinetic curve and the parameters of the conversion function [see eqns. (23), (24) and (26)].

(such as cm) directly on the curve recorded by the experimental device. Figure 2 shows that

$$\frac{m}{n}=\frac{\overline{JK}}{\overline{KL}} \tag{22}$$

$$\frac{(3m-n)T_{1/2}^2}{(3n-m)T_{3/4}^2}=\frac{\overline{FH}}{\overline{AF}} \tag{23}$$

For every pair of points B and G which fulfil the condition $T_B = T_G$, and taking into account eqns. (4) and (11), it is found that

$$\frac{m}{n}=\frac{\log(1-\alpha_B/1-\alpha_G)}{\log(\alpha_G/\alpha_B)} \tag{24}$$

or according to Fig. 2

$$\frac{m}{n}=\frac{\log(\overline{BN}/\overline{GN})}{\log(\overline{MG}/\overline{MB})} \tag{25}$$

This last relationship is useful in checking the constancy of the ratio 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 have a positive slope ($\mathrm{d}T/\mathrm{d}\alpha > 0$), are characterized by a conversion function of the form

$$\mathrm{f}(\alpha)=(1-\alpha)^n;\ m=0 \tag{26}$$

For this case ($m=0$) eqns. (16) and (17) become

$$\frac{\mathrm{d}T}{\mathrm{d}\alpha}=\frac{RT^2}{E}\frac{n}{1-\alpha} \tag{27}$$

$$\frac{\mathrm{d}^2T}{\mathrm{d}\alpha^2}=\frac{RT^2n}{E(1-\alpha)^2}\left(\frac{2RTn}{E}+1\right) \tag{28}$$

The parameter n can be estimated from eqn. (27) using the measured slope of the isokinetic curve for a given value of the degree of conversion. So for the half conversion, one gets

$$n=\frac{E}{2RT_{1/2}^2}\left(\frac{\mathrm{d}T}{\mathrm{d}\alpha}\right)_{1/2} \tag{29}$$

The lack of a minimum on the curve T vs. α ($\alpha_{\min}\rightarrow 1$) together with a negative slope ($\mathrm{d}T/\mathrm{d}\alpha < 0$) means that $n=0$ and the decomposition can be described kinetically by

$$\mathrm{f}(\alpha)=\alpha^m;\ n=0 \tag{30}$$

The particular forms of eqns. (16) and (17) for the conditions in eqn. (30) are

$$\frac{\mathrm{d}T}{\mathrm{d}\alpha}=-\frac{RT^2m}{E\alpha} \tag{31}$$

$$\frac{d^2T}{d\alpha^2} = \frac{RT^2m}{E\alpha^2}\left(\frac{2RTm}{E} + 1\right) \tag{32}$$

The parameter m can be estimated from half conversion data using the relationship

$$m = -\frac{E}{2RT_{1/2}^2}\left(\frac{dT}{d\alpha}\right)_{1/2} \tag{33}$$

With the known values of E, m and n, the pre-exponential factor, A, can be calculated using eqn. (4).

RESULTS AND DISCUSSION

The method of isokinetic curves simplifies considerably the treatment of the experimental data for the valuation of the kinetic parameters but raises difficult experimental problems. According to our information, a thermobalance which records the TG curves in strictly isokinetic conditions has not yet been built. The only device which fulfils this requirement to a certain extent is the Derivatograph Paulik–Paulik-Erdey Q-1500 D [5–7], which was used by us to record the isokinetic TG curves.

The experimental isokinetic TG curve for the dehydration of monohydrated calcium oxalate

$$Ca(COO)_2 \cdot H_2O_{(s)} \rightarrow Ca(COO)_{2(s)} + H_2O_{(g)} \tag{II}$$

is given in Fig. 3 (1). The operating conditions used to obtain the curve were: sample weight $m = 0.1059$ g; applied reaction rate $dm/dt = 0.2$ mg min^{-1}; heating rate until the isokinetic region $dT/d\alpha = 3$ K min^{-1}; initial voltage $U_0 = 75$ V; flat platinum crucible of weight $m_c = 0.740$ g; temperature scale 250°C.

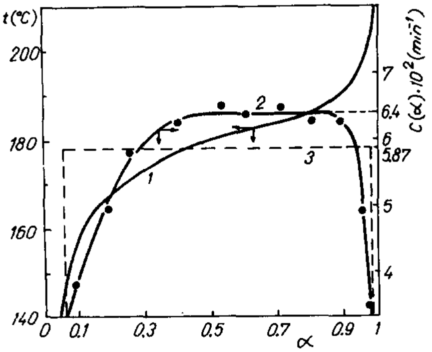

Fig. 3. 1, The experimental isokinetic curve for the dehydration of $Co(COO)_2 \cdot H_2O$; 2, the curve $C(\alpha)$; 3, the plot of C_α vs. conversion degree.

To check the extent of fulfilment of the isokinetic condition the curve $C(\alpha)$ has been given (curve 2) in the same figure. The mean value c_α of the dehydration rate with respect to α (the straight line, 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 a time interval $\Delta t = 0.1$ min. In order to calculate the mean value of the dehydration rate we used the formula

$$\bar{C}_\alpha = \frac{1}{\alpha_2 - \alpha_1} \int_{\alpha_1}^{\alpha_2} C(\alpha)\,\mathrm{d}\alpha \tag{34}$$

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

(I) $0 \leqslant \alpha \leqslant 0.4$; region of linear heating; $\mathrm{d}T/\mathrm{d}\alpha = 3$ K min^{-1}; $0 \leqslant \mathrm{d}\alpha/\mathrm{d}t \leqslant 6.4 \times 10^{-2}$ min^{-1},

(II) $0.4 \leqslant \alpha \leqslant 0.9$; isokinetic region with variable heating rate; $0 \leqslant \mathrm{d}T/\mathrm{d}t \leqslant 3$ K min^{-1}; $\mathrm{d}\alpha/\mathrm{d}t = 6.4 \times 10^{-2}$ min^{-1},

(III) $0.9 \leqslant \alpha \leqslant 1$; region of linear heating; $0 \leqslant \mathrm{d}\alpha/\mathrm{d}t \leqslant 6.4 \times 10^{-2}$ min^{-1}; $\mathrm{d}T/\mathrm{d}t = 3$ K min^{-1}.

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

To estimate the kinetic parameters it is necessary to record at least two isokinetic curves. Such curves for the calcium oxalate dehydration are given in Fig. 4. These curves are characterized by $C_1 = 5.9 \times 10^{-2}$ min^{-1}, $C_2 = 8.6 \times 10^{-2}$ min^{-1}, and half conversion temperatures $t_1 = 180$°C, $t_2 = 186$°C. 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

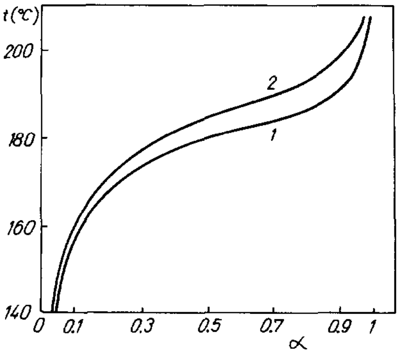

Fig. 4. The changes of the shape and position of the experimental quasi-isokinetic curves with the decomposition rate c for dehydration of $\mathrm{Co(C_2O_4)_2 \cdot H_2O}$. 1, $\bar{C} = 5.1 \times 10^{-2}$ min^{-1}; 2, $\bar{C} = 8.6 \times 10^{-2}$ min^{-1}.

experimental curves. Comparison of Figs. 4 and 1a shows that the shape of the initial region of the experimental curves is different from that corresponding to the isokinetic theoretical 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 eqns. (20), (29) and (5) leads to the following values of the kinetic parameters, which are compared with those obtained by using other methods.

Isokinetic method	Hyperbolic heating method [8]	ATD method [8]
$n = 1.15$ $E = 26$ kcal mole^{-1} $A = 7.5 \times 10^9$ s^{-2}	$n = 1$ $E = 23.5$ kcal mole^{-1} $A = 8 \times 10^6$ s^{-1}	$n = 1$ $E = 21.8$ kcal mole^{-1} $A = 6.23 \times 10^6$ s^{-1}

Generally, the isokinetic method leads to slightly higher values of the kinetic parameters. Like all the non-isothermal methods, the isokinetic method leads to results which are altered to some extent by mass and heat transfer phenomena. So for a sample with the weight $m = 300$ mg in the usual crucible for derivatography, the partial pressure of water being close to the atmospheric pressure, the experimental value obtained for the activation energy is $E = 97$ kcal mole^{-1}. 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 eqn. (4) the increase of the activation energy is going to be compensated mainly by the increase of the pre-exponential factor ($A = 2.8 \times 10^{38}$ s^{-1}) and to a lesser 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 the position of the curve is no longer influenced by the reaction rate value. From a kinetic standpoint [see eqn. (27)] this trend to zero of the isokinetic curve means $E \rightarrow 0$ and $n \rightarrow 0$. In such conditions the position and shape of the isokinetic curve is no longer conditioned by the chemical reaction but by a mass transfer phenomenon which consists of the diffusion of the water vapours from the sample to the surroundings. The increase of the apparent activation energy values with the increase of the partial pressure of the volatile component was reported a long time ago for the isothermal decomposition of some carbonates. This increase, known as the Zawadski–Bretszneider effect [9,10], can be explained taking into account the change of equilibrium pressure with the temperature.

In spite of the limitations inherent in the non-isothermal methods, related to mass and heat transfer phenomena [11] as well as to the use of Arrhenius equation [12] in our opinion and experience these methods can offer useful information concerning the mechanism of the thermal decompositions. To illustrate this statement the isokinetic curve for decomposition of a sample of $KMn0_4$ with weight m = 0.2194 g is given in Fig. 5. The same operating conditions as for the dehydration of $Co(C_20_4) \cdot H_20$ were used, the only

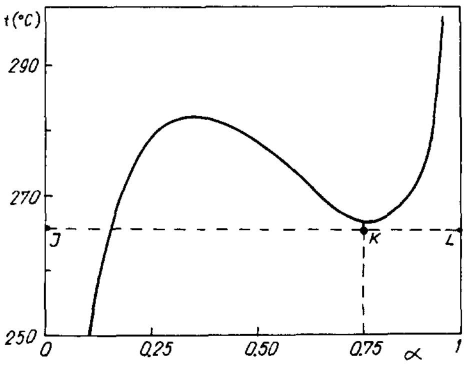

Fig. 5. The quasi-isokinetic experimental curve for the decomposition of $KMn0_4$.

difference being that we used a covered crucible to avoid weight losses due to decrepitation of $KMn0_4$ crystals. The minimum point exhibited by the curve T vs. α indicates an autocatalytic reaction whose kinetics are described by a conversion function of the form given in eqn. (11) with $m \neq 0$ and $n \neq 0$. The autocatalytic character of the $KMn0_4$ decomposition was revealed in a lot of isothermal studies [4,13 and 14]. The curve from Fig. 5 is distorted due to the inertia of the thermoregulator as well as to the mass and heat transfer phenomena so that the condition $d\alpha/dt = C$ is fulfilled only in a very narrow interval of conversion ($0.42 \leqslant \alpha \leqslant 0.69$). In such conditions the kinetic parameters E, m, n and A cannot be determined. Indeed, the use of eqn. (22) leads to

$$\frac{m}{n} = \frac{0.75}{0.25} = 3$$

which is higher than the corresponding value for a symmetrical curve ($m = 1$, $n = 1$) described by the equation of Prout and Tompkins and reported in the literature for this reation [4]. Thus, for the $KMn0_4$ decomposition, the isokinetic method can only establish the general form of the conversion function.

CONCLUSIONS

A general method was suggested for determination of the kinetic parameters of the solid–gas decompositions through recording the α vs. T curves in isokinetic conditions.

The advantages of the isokinetic method are

(a) the activation energy can be determined without taking into account the analytical form of the conversion function and

(b) the form of the conversion function can be established from the shape of the isokinetic curve.

The disadvantages are due to the necessity of complicated experimental devices which can keep the decomposition rate at a given constant value as well as to the mass and heat transfer phenomena which can alter the values of the kinetic parameters.

The advantages and disadvantages of the method have been tested with the help of some theoretically calculated isokinetic curves and also by the experimental isokinetic curves for the heterogeneous dehydration and decomposition of $CoC_2O_4 \cdot H_2O$ and $KMnO_4$.

REFERENCES

1 A.W. Coats and P.J. Redfern, Nature (London), 201 (1964) 68.
2 D. Fătu and E. Segal, Rev. Roum. Chim. 16 (1971) 343.
3 E. Segal and V. Marcu, Thermochim. Acta, 24 (1978) 178.
4 P.W.M. Jacobs and F.C. Tompkins, in W.E. Garner (Ed.), Chemistry of the Solid State, Butterworths, London, 1955, p. 197.
5 F. Paulik and J. Paulik, Anal. Chim. Acta, 60 (1972) 127.
6 F. Paulik and J. Paulik, Proc. 3rd Int. Conf. Therm. Anal., Davos, Vol. 1, (1972), p. 161.
7 F. Paulik and J. Paulik, Hung. Sci. Instr., 38 (1976) 17.
8 D. Fătu, J. Therm. Anal., 1 (1969) 285.
9 J. Zawadski and S. Bretszneider, Z. Electrochem., 41 (1935) 215.
10 M.M. Pavlincenko and E.A. Prodan, Dokl. Akad. Nauk SSSR, 136 (1961) 651.
11 M. Arnold, G.E. Veress, J. Paulik and F. Paulik, J. Therm. Anal., 17 (1979) 507.
12 M. Arnold, G.E. Veress, J. Paulik and F. Paulik, Anal. Chim. Acta, 124 (1981) 341.
13 S.Z. Roghinski, Gheteroghennîi Kataliz, Nauka, Moscow, 1979, p. 180.
14 D. Fătu, Rev. Roum. Chim. 23, (1978) 1029.