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SIMPLE g(α) NON DEPENDENT METHOD TO SOLVE THE KINETIC PARAMETERS BY ISOTHERMAL THERMOGRAVIMETRY

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ABSTRACT

In a previous work [1], we presented the demonstration of the relationship between the activation energy value and the square of the temperature, and the slope of a non-isothermal thermogram. We present in this work, following similar arguments, a coherent demonstration with conclusions, that the relationship between E_a and the square of the temperature occurs under isothermal conditions, too. It can be demonstrated too, that E_a depends on the relative slope of at least two isothermal runs. We conclude that there is complete independence of the E_a and the g(α) value for the isothermal conditions. From the results, a simple graphical–numerical method, based on isothermal thermogravimetry, is proposed to solve and calculate the kinetic parameters E_a, $K(T)$, and K_0 and the kinetic model in a very easy and accurate way.

INTRODUCTION

The determination of the kinetic parameters (E_a, $K(T)$, K_0), using thermogravimetry was carried out using the general equation for reactions in the solid state [2]

$$g(\alpha) = \int_{T_1}^{T_2} K(T)\, dt$$

This equation can be solved under isothermal conditions as

$$g(\alpha) = K(T)t$$

Solving this equation for each g(α) and the possible values of n, a series of values of $K(T)$ is found. Then, through the Arrhenius law it is possible to find a value of E_a for each g(α) and order. In order to find the kinetic mechanism, the isothermal E_a values are usually compared with the non-isothermal E_a values and the model with best agreement is proposed. Done in this way, the calculation is long and needs computational aid. A detailed study of the results obtained using this method, with the main g(α) (nucleation, nucleation–growth, difussion models) (Table 1), offers apparently

TABLE 1

Kinetic functions g(α), in their integral form

Mechanism	g(α)	Designation
Nucleation controlled		
Power law	$\alpha^{1/n}$	$n=1$: zero order $n=0.5$: D1
Growth controlled	$[1-(1-\alpha)^{1-n}]/(1-n)$	$n=0$: zero order $n=1/2$: R2 $n=2/3$: R3 $n=1$: F1
Nucleation – growth controlled		
Avrami–Erofeev	$[-\ln(1-\alpha)]^{1/n}$	$n=1$: F1 $n=2$: A2 $n=3$: A3
Diffusion controlled		
One-dimensional	α^2	D1
Two-dimensional	$\alpha+(1-\alpha)\ln(1-\alpha)$	D2
Three-dimensional	$[1-(1-\alpha)^{1/3}]^2$	D3
Three-dimensional	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	D4

surprising results to us: the E_a values obtained are virtually independent of the equation and order used. These results have been checked out by us with several products [3]. Criado et al. [4] reach the same conclusions using semiempirical arguments. This coincidence of results has led us to try the general resolution of the method used till now, in order to give a mathematical demonstration of these results. In this work we develop several expressions that permit us to check out the relationship between the E_a and the square of the temperature of the process (already demonstrated for non-isothermal conditions), and the relationship between E_a and the relative slope of at least two isothermal measurements. The same expressions show us, that the E_a is independent of g(α) (and consequently of the kinetic model), while $K(T)$ and K_0 are completely dependent on g(α).

RESULTS AND DISCUSSION

For the resolution of the calculations we have used the two extreme points of the region usually considered in kinetic work, that is $\alpha = 0.2$ and $\alpha = 0.8$.

Relationship between E_a *and* Δt

Figure 1 shows us two idealized isothermal thermograms, for the temperatures T_1 and T_2 and their corresponding Δt_1 and Δt_2.

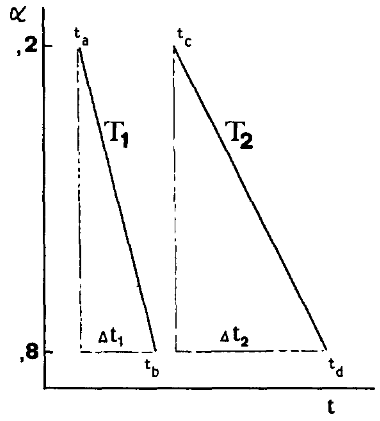

Fig. 1. Idealized isothermal runs at T_1, T_2. (See text.)

According to the general equation $g(\alpha) = K(T)t$, we can write

$$\left.\begin{array}{l} g(\alpha_{0.2}) = K(T_1)t_a \quad (1) \\ g(\alpha_{0.8}) = K(T_1)t_b \quad (2) \end{array}\right\} \text{Thermogram at } T_1$$

and

$$\left.\begin{array}{l} g(\alpha_{0.2}) = K(T_2)t_c \quad (3) \\ g(\alpha_{0.8}) = K(T_2)t_d \quad (4) \end{array}\right\} \text{Thermogram at } T_2$$

$K(T_1)$ can be obtained from (1) and (2), and $K(T_2)$ from (3) and (4)

$$K(T_1) = g(\alpha_{0.8}) - g(\alpha_{0.2})/(t_b - t_a) \qquad (5)$$

$$K(T_2) = g(\alpha_{0.8}) - g(\alpha_{0.2})/(t_d - t_c) \qquad (6)$$

By deriving the ratio (5)/(6), we obtain the important relation

$$K(T_2)/K(T_1) = \Delta t_2/\Delta t_1 \qquad (7)$$

Applying the Arrhenius law at both isothermals, we obtain

$\ln K(T_1) = \ln K_0 - E_a/RT_1$ *and* $\ln K(T_2) = \ln K_0 - E_a/RT_2$

Substracting both equations, we obtain

$$\ln[K(T_1)/K(T_2)] = E_a/R(1/T_2 - 1/T_1)$$

Rearranging and substituting $K(T_1)/K(T_2)$ by their value (7), results

$$E_a = RT_1T_2 \ln(\Delta t_2/\Delta t_1)/(T_1 - T_2) \qquad (8)$$

This equation shows us all the conclusions that have been indicated before: E_a depends on the product T_1T_2, that is, on the square of the temperature. It shows, too, the relationship between E_a and the natural log of the ratio of the Δt values between $\alpha = 0.2 - 0.8$ of the thermograms used. There is no reference to $g(\alpha)$ in the determination of the E_a value. The

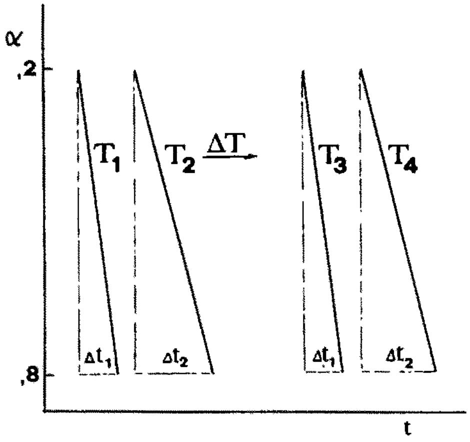

Fig. 2. Two systems of two idealized parallel thermograms with the same Δt, at different temperatures.

expressions (5) and (6) show that the only parameters dependent on $g(\alpha)$ are $K(T)$ and K_0.

Expression (8) can be presented in different ways that will let us make new considerations.

Rearranging, we obtain

$$\Delta t_2 = \Delta t_1 \, e(E_a(T_1 - T_2)/RT_1T_2) \tag{9}$$

that lets us calculate Δt easily for a new T_2, from the previously calculated E_a value and from an isothermal run of reference.

From (9), we obtain

$$\ln \Delta t_2 = (\ln t_1 - E_a/RT_1) + E_a/RT_2 \tag{10}$$

that demonstrates that for a given E_a, the reacting time at different temperatures shows a logarithmical relation versus $1/T$, ($\ln t_1 - E_a/RT_1$ is a constant value).

Equation (10) can be obtained by substitution of (5) in the Arrhenius law.

Relation between the E_a *and the* T

If we present now, two isothermal runs at the temperatures T_1, T_2 and two isothermal runs, parallel at the temperatures T_3, T_4 (Fig. 2), by applying eqn. (8), these new expressions are obtained.

$$E_{a_1} = \text{Constant} \times T_1T_2 \text{ and } E_{a_2} = \text{Constant} \times T_3T_4$$

in which the constant value is the same (dependent only on their ΔT, Δt that will be equal because they are parallel systems). By deriving the ratio of both expressions we obtain

$$E_{a_2} = E_{a_1}T_3T_4/T_1T_2$$

This expression is identical to eqn. (7) or our previous work [1] for the non-isothermal conditions, and it demonstrates the coherence of the system presented.

GENERAL RESOLUTION OF E_a IN ISOTHERMAL CONDITIONS

From eqn. (10), may be written

$\ln \Delta t = E_a/RT + a_0$ where $a_0 = \ln t_1 - E_a/RT_1$

Plotting $\ln \Delta t$ versus $1/T$, for the different isothermal measurements we obtain from the slope of the plot, the E_a value, while

$a_0 = \ln\{[g(\alpha_{0.8}) - g(\alpha_{0.2})]/K_0\}$

Now, we have found the E_a value, but we still have to determine all the other parameters and kinetic characteristics, that is, $K(T)$, K_0 and the accurate model.

For any sort of isothermal run, we have

$g(\alpha_{0.2}) = K(T)t_{0.2}$ and $g(\alpha_{0.8}) = K(T)t_{0.8}$

Deriving the ratio, we obtain

$$g(\alpha_{0.2})/g(\alpha_{0.8}) = t_{0.2}/t_{0.8} \qquad (12)$$

From the different equations of the Table 1, we can obtain the corresponding values to the ratio of the g(α) mentioned in (12). From the value

TABLE 2

Values of the ratio $g(\alpha_{0.2})/g(\alpha_{0.8})$ and difference $g(\alpha_{0.8})-g(\alpha_{0.2})$, for the kinetic functions of Table 1

Equation	$g(\alpha_{0.2})/g(\alpha_{0.8})$	$g(\alpha_{0.8})-g(\alpha_{0.2})$
Zero order	0.25000	0.60000
R2	0.19098	0.89443
R3	0.17265	1.03054
F1	0.13865	1.38629
A2	0.37235	0.79626
A3	0.51757	0.56536
D1	0.06250	0.60000
D2	0.04494	0.45663
D3	0.02981	0.16725
D4	0.03925	0.11978
Power law		
$n = 0.5$	0.06250	0.60000
$n = 1.0$	0.25000	0.60000
$n = 1.5$	0.39685	0.51978

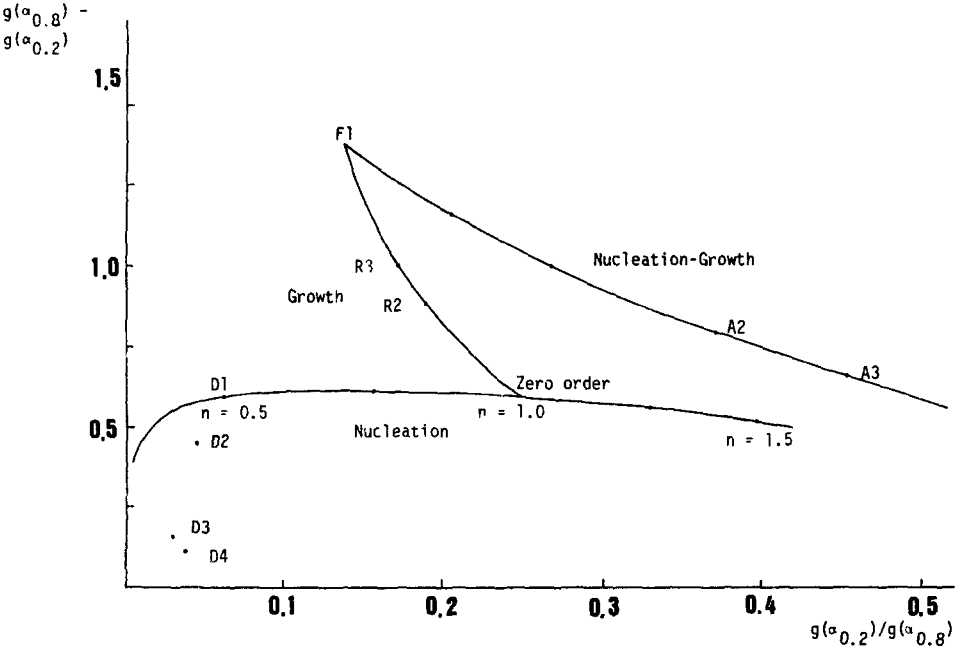

Fig. 3. Plot of $g(\alpha_{0.2})/g(\alpha_{0.8})$ vs. $g(\alpha_{0.8})-g(\alpha_{0.2})$, for the principal kinetic models.

$t_{0.2}/t_{0.8}$ (that has to be constant for any isothermal run of a product), and the best agreement between the possible theoretical values and the real values, the assignation of the kinetic model can be tried, and the $K(T)$ values as indicated in [5]. In the Table 2, we have listed the values of the ratio and the difference of $g(\alpha)$, and once plotted becomes the Fig. 3. The plot shows that for many values of $t_{0.2}/t_{0.8}$, there is the chance of assigning more than one model. This ambiguity can be solved by proving which of the $K(T)$ and $g(\alpha)$ values obtained graphically, fits better with our experimental thermograms. Finally, the K_0 value, is found from the Arrhenius law.

THEORETICAL TESTING OF THE METHOD

To test rigorously our proposal, we have made two theoretical isothermal curves (for the points $\alpha = 0.2$ and 0.8), for all $g(\alpha)$ of the Table 1, from the arbitrary data given: $T_1 = 475$ K, $T_2 = 525$ K, $E_a = 25\,000$ cal, $K_0 = 10^{10}$ min^{-1}. The corresponding $K(T)$ are obtained from the Arrhenius law, and are indicated too, in the Table 3. Applying the eqn. (8) to the pairs of Δt_1 and Δt_2 values, we obtain as was foreseen, the E_a value of 25 000 cal, independent of the kinetic model. As mentioned above, we test that the ratio

TABLE 3

Fundamental values of t, for two isothermal thermograms, calculated from the principals $g(\alpha)$; the data used are: $E_a = 25$ kcal mol^{-1}, $K_0 = 10^{10}$ min^{-1}, $T_1 = 475$ K, $T_2 = 525$ K (E_a * = calculated value from eqn. (8) and $\Delta t(475)/\Delta t(525)$ for each model)

Equation	$t_{0.2}$	$t_{0.8}$	Δt	$t_{0.2}$	$t_{0.8}$	Δt	E_a *
Zero order	6.0463	25.8498	19.3874	0.5179	2.0717	1.5538	25.000
R2	6.8226	35.7236	28.9010	0.5468	2.8630	2.3162	25.000
R3	6.9487	40.2478	33.2992	0.5569	3.2256	2.6687	25.000
F1	7.2103	52.0046	44.7943	0.5779	4.1678	3.5900	25.000
A2	15.2637	40.9925	25.7288	1.2233	3.2853	2.0620	25.000
A3	19.5988	37.8668	18.2681	1.5707	3.0348	1.4641	25.000
D1	1.2925	20.6799	19.3874	0.1036	1.6574	1.5538	25.000
D2	0.6942	15.4489	14.7547	0.0556	1.2381	1.1825	25.000
D3	0.1660	5.5702	5.4042	0.0133	0.4464	0.4331	25.000
D4	0.1581	4.0284	3.8703	0.0127	0.3228	0.3102	25.000
Power law							
$n = 0.5$	1.2925	20.6799	19.3874	0.1036	1.6574	1.5538	25.000
$n = 1.0$	6.0463	25.8498	19.3874	0.5179	2.0717	1.5538	25.000
$n = 1.5$	11.0506	27.8459	16.7952	0.8856	2.2316	1.3460	25.000
	$T = 475$ K $K(T) = 3.0948 \times 10^{-2}$			$T = 525$ K $K(T) = 0.38616$			

$t_{0.2}/t_{0.8}$ is constant for each $g(\alpha)$, independent of T and the same as the value of $g(\alpha_{0.2})/g(\alpha_{0.8})$, indicated in Table 2.

PRACTICAL TESTING OF THE METHOD

The solid phase thermal deaquation–anation of the compounds $[M(NH_3)_5H_2O][Co(CN)_6]$ has been investigated by means of the method proposed in this work. The results of the isothermal calculations, previously published [4], are shown in the Table 4. In Table 5, the experimental values of T, $t_{0.2}$, $t_{0.8}$, Δt and $t_{0.2}/t_{0.8}$ are shown for the different isothermal runs of these three products. Plotting the ln Δt values versus $1/T$, the Fig. 4 is obtained. The plot parameters are indicated in Table 6.

The E_a value found from graph 3, demonstrates the high accuracy of this method, compared with the rigorous calculation of all the $g(\alpha)$ and orders.

For M = Co, three mechanisms are possible (ratio near 0.17), and for Rh and Ir two mechanisms are possible. To choose the kinetic model, it is necessary to calculate $t_{0.2}$ and $t_{0.8}$ from the general expression $t = g(\alpha)/K(T)$, with the possible $g(\alpha)$ and $K(T)$ (see Table 7).

With this calculation (very short, that can be made with a pocket calculator), the kinetic model that presents a best agreement with the

TABLE 4

Kinetic parameters for the compounds $[M(NH_3)_5H_2O][Co(CN)_6]$, (previously published); the values (*) are those which show the best agreement with the non-isothermal data

		Growth			Nucl.–Growth				Power law		
		Zero	R2	R3	F1	$n=1.5$	A2	A3	n = 0.5	$n=1.0$	$n=1.5$
M = Co	E_a	126.5	126.4	126.5	126.9	127.2 *	127.5	127.9	124.9	126.5	127.5
	ln K_0	27.361	27.566	27.944	28.311	28.043 *	27.886	27.655	26.966	26.361	27.475
M = Rh	E_a	115.1	115.8	116.7	117.6	116.6*	116.1	115.7	116.5	115.1	114.4
	ln K_0	25.207	25.613	26.198	26.671	26.095 *	25.732	25.258	25.614	25.207	24.910
M = Ir	E_a	89.0	87.7	85.4	83.5	86.8	87.8	87.8 *	85.6	89.0	89.9
	ln K_0	18.363	18.202	18.900	17.599	17.950	18.005	17.917 *	17.390	18.362	18.448

	Model	$K(T)$	$K(T)$	$K(T)$	$K(T)$	$K(T)$
M = Co	Nuc.–Gr.	438 K	440.5 K	443 K	445.5 K	448 K
	$n=1.5$	5.961×10^{-2}	7.045×10^{-2}	9.206×10^{-2}	0.1064	0.1284
M = Rh	Nuc.–Gr.	443 K	445.5 K	448 K	450.5 K	453 K
	$n=1.5$	0.2365	0.2539	0.2972	0.3884	0.4567
M = Ir	Nuc.–Gr.	448 K	450.5 K	453 K	455.5 K	458 K
	$n=3$	0.2233	0.2509	0.2829	0.3323	0.3690

TABLE 5

Fundamental values for the experimental isothermal runs for the compounds $[M(NH_3)_5H_2O][Co(CN)_6]$

M	T(K)	$t_{0.2}$	$t_{0.8}$	Δt	$t_{0.2}/t_{0.8}$
Co	438	3.25	19.68	16.43	0.1652
	440.5	2.70	16.80	14.10	0.1607
	443	2.10	12.50	10.40	0.1680
	445.5	1.90	11.10	9.20	0.1712
	448	1.70	9.30	7.60	0.1828
Rh	443	1.14	5.31	4.17	0.2147
	445.5	1.38	5.18	3.80	0.2657
	448	1.44	4.68	3.24	0.3075
	450.5	1.15	3.66	2.51	0.3142
	453	1.10	3.26	2.16	0.3374
Ir	448	2.36	5.09	2.73	0.4644
	450.5	2.14	4.55	2.41	0.4698
	453	1.89	3.99	2.10	0.4734
	455.5	1.66	3.52	1.86	0.4716
	458	1.55	3.21	1.66	0.4825

experimental value of the ratio $t_{0.2}/t_{0.8}$ is assigned. Table 8 shows the values obtained by this method and the comparison with the values previously published. The comparison of the results with the experimental values (Table 5), shows the greater exactitude of the new calculation.

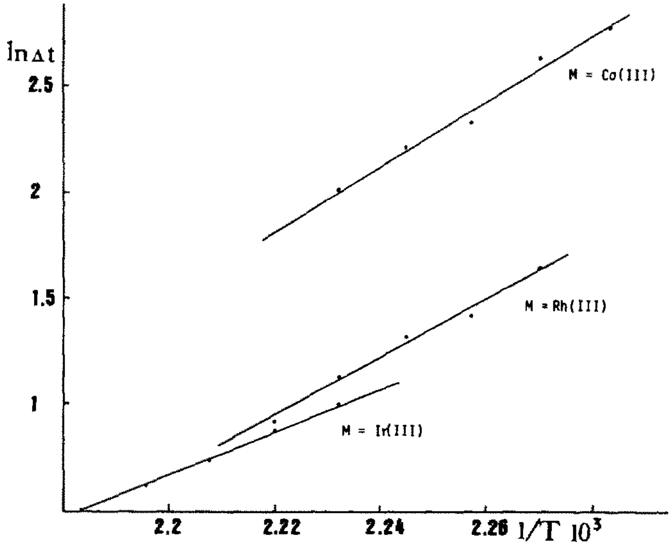

Fig. 4. Plot of ln Δt vs. $1/T$ (eqn. (10)), for the compounds $[M(NH_3)_5H_2O][Co(CN)_6]$. The slope gives the E_a value.

TABLE 6

Parameters obtained from the plots ln t vs. $1/T$, corresponding to Fig. 4, and E_a value derived from a_1

M = Co(III)	
$a_1 = 15.4544$	$r^2 = 0.9922$
$a_0 = -32.481$	$E_a = 128.3$ kJ mol^{-1}
M = Rh(III)	
$a_1 = 13.8603$	$r^2 = 0.9882$
$a_0 = -29.814$	$E_a = 115.1$ kJ mol^{-1}
M = Ir(III)	
$a_1 = 10.2411$	$r^2 = 0.9996$
$a_0 = -21.857$	$E_a = 85.0$ kJ mol^{-1}

TABLE 7

$K(T)$ and K_0 values for $[M(NH_3)_5H_2O][Co(CN)_6]$, obtained in this work (see comparison with Table 4)

T(K)	M = Co		M = Rh		M = Ir	
	$K(T)$	ln K_0	K(T)	ln K_0	$K(T)$	ln K_0
438	7.824×10^{-2}	28.641	–	–	–	–
440.5	9.117×10^{-2}	28.593	–	–	–	–
443	0.1236	28.700	0.2313	25.729	–	–
445.5	0.1397	28.626	0.2538	25.646	–	–
448	0.1692	28.624	0.2977	25.632	0.2429	17.351
450.5	–	–	0.3843	25.716	0.2751	17.394
453	–	–	0.4465	25.696	0.3158	17.361
455.5	–	–	–	–	0.3565	17.358
458	–	–	–	–	0.3995	17.350

TABLE 8

Fundamental values of t for the isothermal runs of $[M(NH_3)_5H_2O][Co(CN)_6]$ [a]

M	T(K)	$t^*_{0.2}$	$t^*_{0.8}$	Δt^*	$t^*_{0.2}/t_{0.8}$	$t^{**}_{0.2}$	$t^{**}_{0.8}$	Δt^{**}	$t^{**}_{0.2}/t_{0.8}$
Co	438	3.34	19.77	16.43	0.1689	6.18	23.06	16.88	0.2680
	440.5	2.87	16.97	14.10	0.1691	5.22	19.49	14.27	0.2678
	443	2.12	12.52	10.40	0.1693	4.00	14.92	10.92	0.2682
	445.5	1.87	11.07	9.20	0.1689	3.46	12.90	9.44	0.2682
	448	1.55	9.15	7.60	0.1694	2.87	10.70	7.83	0.2682
Rh	443	1.67	5.84	4.17	0.2860	1.56	5.83	4.27	0.2676
	445.5	1.52	5.32	3.80	0.2857	1.45	5.41	3.96	0.2680
	448	1.30	4.54	3.24	0.2863	1.24	4.62	3.38	0.2684
	450.5	1.01	3.52	2.51	0.2869	0.95	3.54	2.59	0.2684
	453	0.87	3.03	2.16	0.2871	0.81	3.01	2.20	0.2691
Ir	448	2.45	5.18	2.73	0.4730	2.60	5.32	2.72	0.4887
	450.5	2.16	4.57	2.41	0.4726	2.31	4.74	2.43	0.4873
	453	1.88	3.98	2.10	0.4724	2.05	4.20	2.15	0.4881
	455.5	1.67	3.53	2.86	0.4731	1.74	3.58	1.84	0.4860
	458	1.49	3.15	1.66	0.4730	1.57	3.22	1.65	0.4876

[a] * This work. ** Previously calculated values. ** This work. The comparison of the values obtained in this work with those given in Table 5, shows the greater accuracy of our new method.

CONCLUSIONS

The method presented lets us calculate, in an easy and accurate way, the kinetic parameters E_a, $K(T)$, K_0 and the kinetic model, in isothermal conditions. The main advantage of this system is that it permits the resolution, in just a few minutes and with a pocket calculator, instead of the calculation with computers that is used in the classical system. It only requires the measurements of two experimental points. It permits us to control the reaction if the measurements are correct while making the runs, by the control of the constant value $t_{0.2}/t_{0.8}$.

It is demonstrated that there is non dependence of E_a and $g(\alpha)$. It is corroborated that the comparison with a non-isothermal run, is not necessary to determine the kinetic model. It is evident that the kinetic parameters can be calculated with two isothermal runs or with an isothermal run (that gives the correct $g(\alpha)$), and another non-isothermal run (see ref. 1).

REFERENCES

1 J. Ribas, M. Serra and A. Escuer, Thermochim. Acta, 91 (1985) 107.

2 C.H. Bamford, and C.F.H. Tipper (Eds.), Comprehensive Chemical Kinetics, Vol. 22, Reactions in the Solid State, Elsevier, Amsterdam, 1980, Chap. 3.

3 M. Monfort, M. Serra, A. Escuer and J. Ribas, Thermochim. Acta, 69 (1983) 397; M. Corbella, C. Diaz, A. Escuer, A. Seguí and J. Ribas, Thermochim. Acta, 74 (1984) 23; J. Ribas, A. Escuer and M. Monfort, Thermochim. Acta, 76 (1984) 201; J. Ribas, M. Serra and A. Escuer, Thermochim. Acta, 80 (1984) 103; J. Ribas, M. Serra and A. Escuer, Inorg. Chem., 1984 23 (2236).

4 J.M. Criado, M. Gonzalez, A. Ortega and C. Real, J. Therm. Anal., 29 (1984) 243.

5 J. Ribas, A. Escuer, M. Monfort, Thermochim. Acta, 76 (1984) 201.