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SIMPLE NUMERICAL AND GRAPHICAL METHOD TO SOLVE THE KINETIC PARAMETERS BY DYNAMIC THERMOGRAVIMETRY

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ABSTRACT

A simple graphical–numerical method, based on dynamic thermogravimetry, is proposed to solve and calculate the activation energy of solid-phase reactions. The method gives, very easily and with remarkable accuracy (deviation less than 5%) compared with the sophisticated calculation of the Coats and Redfern's equation, the activation energy for the different $g(\alpha)$ functions.

INTRODUCTION

The determination of the kinetic parameters (E_a, k_0, n) using thermogravimetry was carried out using the general equation for reactions in the solid state [1]

$$g(\alpha)=\int_{T_0}^{T_1} k(T)\mathrm{d}t$$

This equation can be solved under isothermal [$g(\alpha)=kt$] or dynamic conditions. In the latter case, the integral cannot be solved exactly and several approximations have been given in the literature. Using the more common Coats and Redfern approximation [2], we have

$$\ln g(\alpha)/T^2=\ln K_0R/\beta E_a(1-2RT/E_a)-E_a/RT \qquad (1)$$

For each $g(\alpha)$ (Table 1) and n value, a program must be developed in order to obtain accurate results. Bearing in mind that the solution of the kinetic problems by dynamic TG is not unique (an isothermal treatment is necessary) we have attempted to replace this complicated mathematical process by a more simple but accurate enough method.

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TABLE 1

Kinetic functions, g(α), used in their integral form

Mechanism	g(α)
Nucleation controlled	
Exponential law	$\ln \alpha^n$
Power law	$\alpha^{1/n}$
Growth controlled	$[1-(1-\alpha)^{1-n}]/(1-n)$
for $n=1$	$[-\ln(1-\alpha)]$
Nucleation-Growth controlled	
Avrami–Erofeev	$[-\ln(1-\alpha)]^{1/n}$
Prout–Tompkins	$\ln[\alpha/(1-\alpha)]$
Diffusion controlled	
One-dimensional	α^2
Two-dimensional	$\alpha+(1-\alpha)\ln(1-\alpha)$
Three-dimensional	$[1-(1-\alpha)^{1/3}]^2$
Three-dimensional	$(1-2/3\alpha)-(1-\alpha)^{2/3}$

In this work we develop several expressions which relate E_a with the temperature at $\alpha = 0.5$ and with ΔT between $\alpha = 0.2$ and 0.8 (rate of the process). From these data, E_a can be calculated by a very simple numerical or graphical method.

RESULTS AND DISCUSSION

All the calculations have been carried out assuming linearity of the part of the thermogram between $0.2 \leqslant \alpha \leqslant 0.8$ (this assumption is valid in most cases). Furthermore, before proceeding to calculate E_a by a graphical method from dynamic TG, the following must be taken into account. The new graphical method is based on the variation of the activation energy of a process with two parameters: the temperature for which $\alpha = 0.5$ (hereafter refered to as T); and the temperature difference between $\alpha = 0.2$ and 0.8. This difference corresponds to the slope of the thermogram and we shall call it ΔT.

We shall now develop a relationship between the E_a value of a process with respect to T and ΔT.

Relationship between E_a *and* T

Figure 1 shows two parallel thermograms with a marked variation (T_1 and T_2). The linearity in this region makes $\Delta T = 2n$. If we now apply the Coats

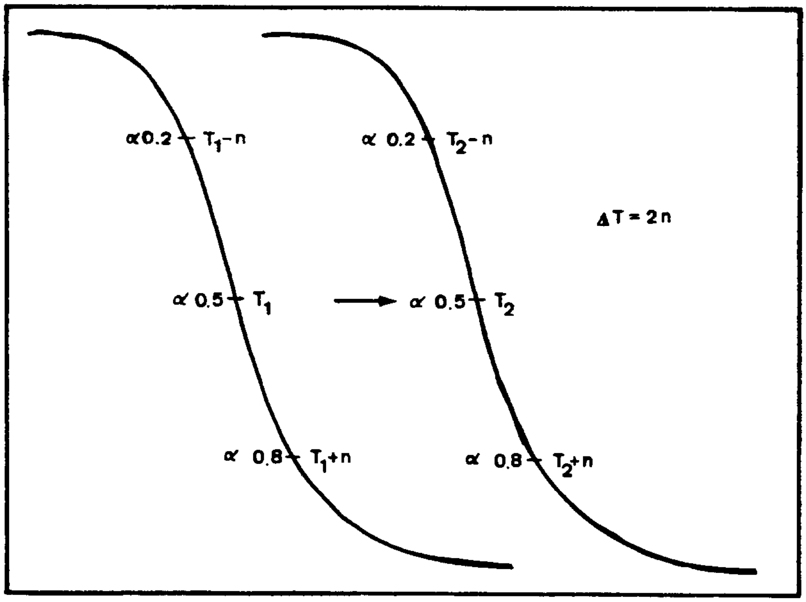

Fig. 1. Two parallel thermograms with different T at $\alpha = 0.5$.

and Redfern equation in an integrated form to the four points for which $\alpha = 0.2$ and 0.8, we obtain

$$\ln g(\alpha_{0.2})/(T_1 - n)^2 = \ln K_{0_1}R/\beta E_{a_1} - E_{a_1}/R(T_1 - n) \tag{2}$$

$$\ln g(\alpha_{0.2})/(T_2 - n)^2 = \ln K_{0_2}R/\beta E_{a_2} - E_{a_2}/R(T_2 - n) \tag{3}$$

$$\ln g(\alpha_{0.8})/(T_1 + n)^2 = \ln K_{0_1}R/\beta E_{a_1} - E_{a_1}/R(T_1 + n) \tag{4}$$

$$\ln g(\alpha_{0.8})/(T_2 + n)^2 = \ln K_{0_2}R/\beta E_{a_2} - E_{a_2}/R(T_2 + n) \tag{5}$$

Subtracting eqns. (2) and (5) from eqns. (3) and (4), and operating, we obtain

$$E_{a_2} = \left\{ E_{a_1}/(T_1^2 - n^2) + R/n \ln[(T_2 - n)(T_1 + n)/(T_1 - n)(T_2 + n)] \right\}(T_2^2 - n^2) \tag{6}$$

The logarithmic term is practically zero in this expression; furthermore, n^2 is also very small in front of T^2. Thus, eqn. (6) becomes

$$E_{a_2}/E_{a_1} = T_2^2/T_1^2 \tag{7}$$

It was found that the error made using these two simplifications, with respect to the general equation, was only about 0.25%.

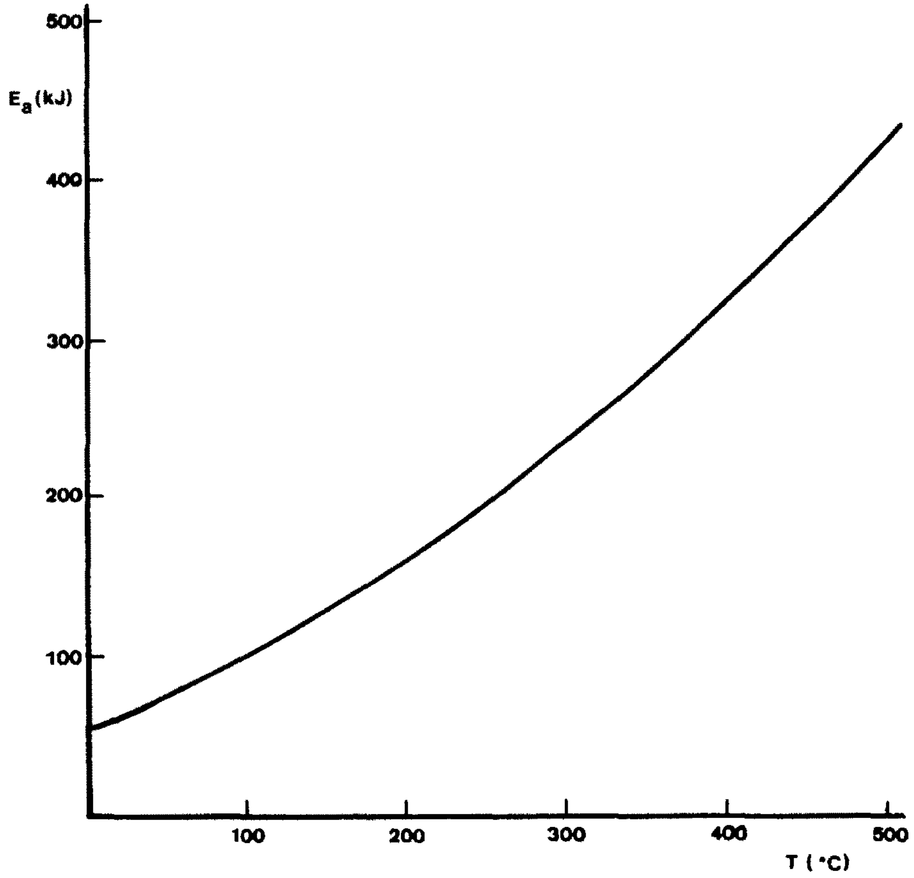

Fig. 2. Parabolic dependence between E_a and T.

On plotting the above equation (7), Fig. 2 (which shows the parabolic dependence between E_a and T) is obtained.

Relationship between E_a *and* ΔT *(rate of the process; slope of the curve)*

To derive this relationship let us take two curves passing through the same point, $\alpha = 0.5$ (identical T), but with a very different slope (the rate of each process is different) (Fig. 3). Let us assume for our calculation that we use a given curve and that the activation energy is known. We are going to find the variation of the activation energy of another process with T_m, on changing the slope (m). Again applying the Coats and Redfern equation to the four points for which $\alpha = 0.2$ and 0.8, we find the following expressions

$$\ln g(\alpha_{0.2})/(T_1 - n)^2 = \ln K_{0_1}R/\beta E_{a_1} - E_{a_1}/R(T_1 - n) \qquad (8)$$

$$\ln g(\alpha_{0.8})/(T_1 + n)^2 = \ln K_{0_1}R/\beta E_{a_1} - E_{a_1}/R(T_1 + n) \qquad (9)$$

$$\ln g(\alpha_{0.2})/(T_2 - m)^2 = \ln K_{0_2}R/\beta E_{a_2} - E_{a_2}/R(T_2 - m) \tag{10}$$

$$\ln g(\alpha_{0.8})/(T_2 + m)^2 = \ln K_{0_2}R/\beta E_{a_2} - E_{a_2}/R(T_2 + m) \tag{11}$$

Subtracting eqns. (9) and (10) from eqns. (8) and (11) and rearranging, we obtain

$$E_{a_2} = \left\{ E_{a_1}n/T_1^2 - n^2 + R \ln\left[(T_2 - m)(T_1 + n)/(T_1 - n)(T_2 + m)\right] \right\} \times \left(T_2^2 - m^2\right)/m \tag{12}$$

This equation cannot be simplified, but obviously the most important factor is m, since this is the only divisor. Therefore, the E_a value of the process with slope m depends essentially on m.

Graphical method

Applying the two above assumptions and using the Coats and Redfern equation to the curve T_m (which is really the unknown), we obtain eqns. (2) and (4). From eqns. (2) and (4) we can find the value of E_a

$$E_a = -R(T^2 - n^2)/2n \ln\left[g(\alpha_{0.2})(T + n)^2/g(\alpha_{0.8})(T - n)^2\right] \tag{13}$$

We can now plot eqn. (13) for each $g(\alpha)$ function given in the literature [1] taking $1/\Delta T$ as ordinate and E_a as the abscissa, but then the plot would not have a general use. In order to obtain a generalized plot, let us assume that

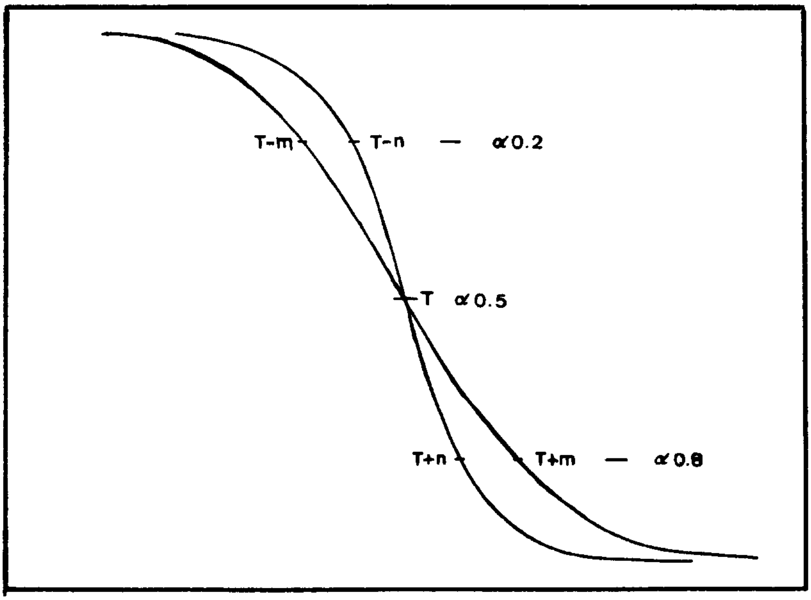

Fig. 3. Two curves with identical T at $\alpha = 0.5$ but different slope.

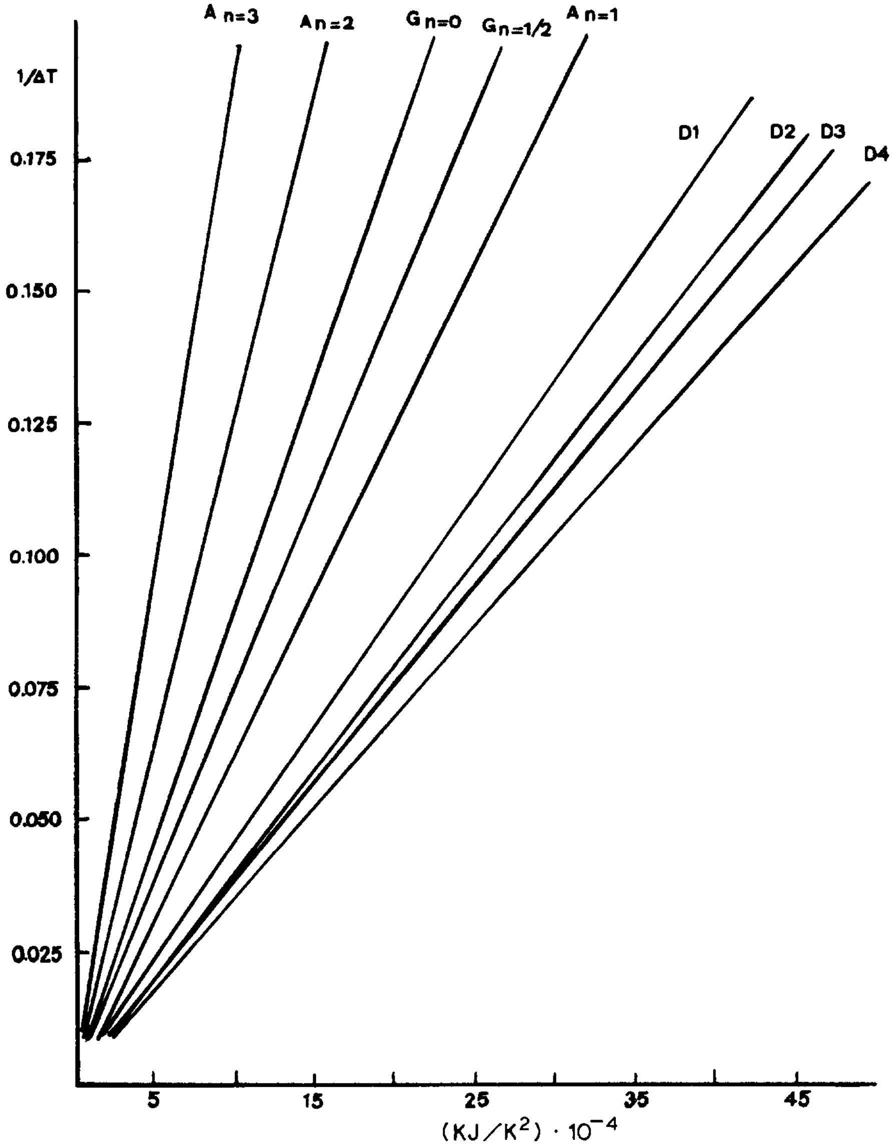

Fig. 4. E_a vs. $1/\Delta T$ for each g(α). A = Avrami model; G = growth model; D = diffusion model.

$T_1 = 100°\text{C}$ (373 K). In this way, any E_a value will be related to the activation energy for $T = 100°\text{C}$ according to eqn. (7). Thus, we should use $E_a/373^2$ rather than E_a as the abscissa; the value found, multiplied by T_2^2, is the real value of E_a (Fig. 4).

In order to draw the plots in the units given, we have previously calculated the equations of the straight lines corresponding to the more usual models and orders of reaction. The corresponding plots ($y = a_1x + a_0$, with $y = 1/T$

TABLE 2

Parameters of the equations of the straight lines corresponding to the following models: D = diffusion; AV = Avrami; GR = growth

Parameters	a_1	a_0	r^2
D1	43.432	2.019×10^{-3}	1.0000
D2	38.802	1.814×10^{-3}	1.0000
D3	37.187	1.723×10^{-3}	1.0000
D4	34.273	1.602×10^{-3}	1.0000
AV3	182.71	8.247×10^{-3}	1.0000
AV2	121.86	5.518×10^{-3}	1.0000
AV1	60.924	2.811×10^{-3}	1.0000
GR0.5	72.717	3.328×10^{-3}	1.0000
GR0	86.866	3.935×10^{-3}	1.0000

and $x = \mathrm{kJ}/373^2$) are given in Table 2. As can be seen, linear regression coefficients, r^2, are always 1.0000.

For a given case, the use of these plots is even more simple than the graphical resolution, since the results can be obtained from the knowledge of T and ΔT for a given dynamic thermogram, with a pocket calculator.

Testing of the method

In order to check the accuracy of the proposed graphical method, we have calculated the values of E_a of several compounds for which we had previi-

TABLE 3

Comparison of results (E_{calc} with the Coats and Redfern method, and E_{graph}) for the model of nucleation–growth (Avrami) with $n = 1$. The left-hand symbol indicates $[M(H_2O)(NH_3)_5]^{3+}$ and the right-hand symbol indicates $[M(CN)_4]^{2-}$ (M = Ni, Pd, Pt) and $[Co(CN)_6]^{3-}$. The calculated E_a values are given in a previous work of the authors [3]

Product	T ($\alpha = 0.2$)	T ($\alpha = 0.5$)	T ($\alpha = 0.8$)	ΔT	$1/\Delta T$	$E_{a(calc)}$	$E_{a(graph)}$	% dif.
Co–Ni	103.5	115	123	19.5	5.128×10^{-2}	123	120	−2.4
Co–Pd	105.5	115	121.5	16	6.250×10^{-2}	156	148	−5.1
Co–Pt	99.5	109	116	16.5	6.061×10^{-2}	141	138	−2.1
Rh–Ni	116.5	122.5	128	11.5	8.696×10^{-2}	227	216	−4.8
Rh–Pd	92	99.5	105	13	7.692×10^{-2}	172	169	−1.7
Rh–Pt	72	81	96	24	4.167×10^{-2}	75	80	+6.7
Ir–Ni	133	140.5	144	11	9.091×10^{-2}	232	247	+6.4
Ir–Pd	126	134	138	12	8.333×10^{-2}	205	218	+6.3
Ir–Pt	98	106	116.5	18.5	5.405×10^{-2}	112	121	+8.0
Co–Co	173	182	190	15	6.667×10^{-2}	199	216	+8.5
Rh–Co	163	174	182	19	5.263×10^{-2}	159	163	+2.5
Ir–Co	174	181.5	185	11	9.091×10^{-2}	314	299	−4.8

TABLE 4

Calculated (Coats and Redfern method) and graphical values of E_a (kJ mol^{-1}) for all g(α) for $[Co(H_2O)(NH_3)_5]_2[Ni(CN)_4]_3$ (Ni–Co): AV = Avrami; GR = growth; D = diffusion

Kinetic model:	AV3	AV2	AV1	GR0.5	GR0	D1	D2	D3	D4
E_a (calc)	37	59	123	84	102	175	197	206	224
E_a (graph)	35.5	56.6	119.8	82.1	99.3	170.8	191.9	200.6	218.2
% dif.	4.0	4.2	2.6	2.3	2.7	2.4	2.6	2.6	2.6

ously calculated their E_a values using the complete Coats and Redfern equation for all g(α) functions and all orders. Table 3 gives the comparison of results for the model of nucleation–growth, with $n = 1$. We have also indicated in Table 4 the calculated values of all g(α) functions for one of the products, $[Co(H_2O)(NH_3)_5]_2[Ni(CN)_4]_3$ (Co–Ni).

CONCLUSIONS

In view of the results, we may conclude that our proposed graphical method is semi-quantitative with few values carrying errors greater than 5%.

Bearing in mind that dynamic TG is only a complementary tool for the resolution of kinetic parameters (the resolution must be carried out using isothermal methods), we believe that the complicated calculations involved in using the Coats and Redfern equation can be replaced by our method. However, as we have indicated, an isothermal calculation is necessary to find the real values of the activation energy.

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