INFLUENCE OF THE MASS AND HEATING RATE IN THE KINETIC PARAMETERS IN SOLID =SOLID+GAS REACTIONS

M. R. ALVAREZ, J. J. ICAZA AND E. H. BOCANEGRA

Facultad de Ciencias, Dto. de Fisica, Univ. Bilbao, Aptd. 644, Bilbao (Spain)

M. J. TELLO

Facultad de Ciencias, Dto. de Fisica, Universidad de Granada (Spain)

(Received 21 December 1974)

ABSTRACT

A study about the influence of the mass and heating rate on the kinetic parameters in solid = solid + gas reactions shows that the low dispersion of the values for activation energy and order parameter support the idea that the use of a small mass is consistent with the theoretical suppositions. This should be taken into account in the diffusion phenomena and temperature gradient involved in the experimental process.

INTRODUCTION

The experimental results about kinetic problems in solid = solid + gas reactions employing thermogravimetric techniques in dynamical as well as isothermal regimes are influenced by experimental conditions. As a consequence, the kinetic parameters obtained are also a function of these experimental conditions.

Different aspects are involved in the general theory about the kinetic equations of the type indicated above: a growing process which is more or less incorporated[1]; a potential homogenization resulting from a diffusion process in which the concentration is a function of the space and time coordinates[1,2]. Therefore, it is necessary to make some simplifications when applying Fick's law. The exchange of energy, that is required to achieve a homogenization temperature in the sample produces a temperature gradient[3], which must be introduced in a kinetic equation of heat conduction of very complex solution[4].

Another experimental condition must be taken into account such as a vacuum or controlled atmosphere (in this case the pressure of gas), the type of the sample (powder or crystal) etc.

In this case, two magnitudes, the mass of the sample and the heating rate are of interest to us in relation with the growing and diffusion process as well as with the temperature gradient[5-9].

In this paper a study about the influence of the sample mass and the heating rate was carried out using a large interval in the heating rate and a small mass. The substance chosen was $C_2O_4Ca \cdot H_2O$ because there are many studies about water loss

for comparison[9-11]. The theoretical interpretation of the thermogrammes was carried out using the Dharwadkar–Karkhanavala (D–K) method[9] as well as the Freeman–Carroll (F–C) method[11]. All the symbols used here were explained already in refs. 9–11.

EXPERIMENTAL

The calcium oxalate monohydrate was of c.p. grade, purchased from the Fisher Scientific Company. No purification was made.

The thermogravimetric traces were obtained in a Perkin-Elmer thermobalance (TGS-1) after calibration with magnetic standards. Thermogravimetric runs were carried out in dry nitrogen with a flow-rate of 25 ml min^{-1} and the mass of the sample as well as the heating rate were varied during the experience. Each run was repeated 2 or 3 times and the experimental reproducibility was good for each mass and heating rate selected.

The initial temperatures of decomposition were confirmed using a Perkin-Elmer DSC calorimeter (DSC-1) with a very good calibration by using ferroelectric standards[12].

TABLE 1

INITIAL AND FINAL TEMPERATURES AS A FUNCTION OF
THE HEATING RATE

Heating rate ($^\circ C\ min^{-1}$)	Initial mass (mg)	Initial temp. ($^\circ C$)	Inflection temp. ($^\circ C$)	Final temp. ($^\circ C$)
1.25	2.50	108	123	128
2.50		100	123	134
5		102	135	147
10		100	140	156
20		113	160	176
40		112	176	193
80		106	193	212
1.25	5	106	125	133
2.50		105	133	142
5		105	137	149
10		104	153	164
20		108	176	192
40		108	194	209
80		110	218	244
1.25	10	98	122	132
2.50		103	140	149
5		103	146	160
10		109	160	180
20		110	175	196
40		115	198	227
80		120	229	261

RESULTS AND DISCUSSION

Table 1 shows the influence of the mass of the sample and the heating rate in the initial, inflexion and final temperature. It can be noted that the initial temperature is approximately constant but the decomposition interval increases when both the mass of the sample and the heating rate increase. The influence of the heating rate is more important than the sample size which is opposite to the D–K experimental results employing a short interval of heating rate and a large mass[9]. Also it must be noted that the initial temperature is lower than in the D–K results[9] but similar with other works[13].

Figure 1 shows a plot of the D–K method for a heating rate of $20°C \, min^{-1}$ and mass of 2.5, 5 and 10 mg, respectively. In this figure the spread of the values obtained for each temperature is pointed out grafically. Similar representations were observed for all other experimental conditions. Also it can be noticed that the beginning of the reaction is characterised by an induction period and as a consequence a higher slope and more spread in the experimental values.
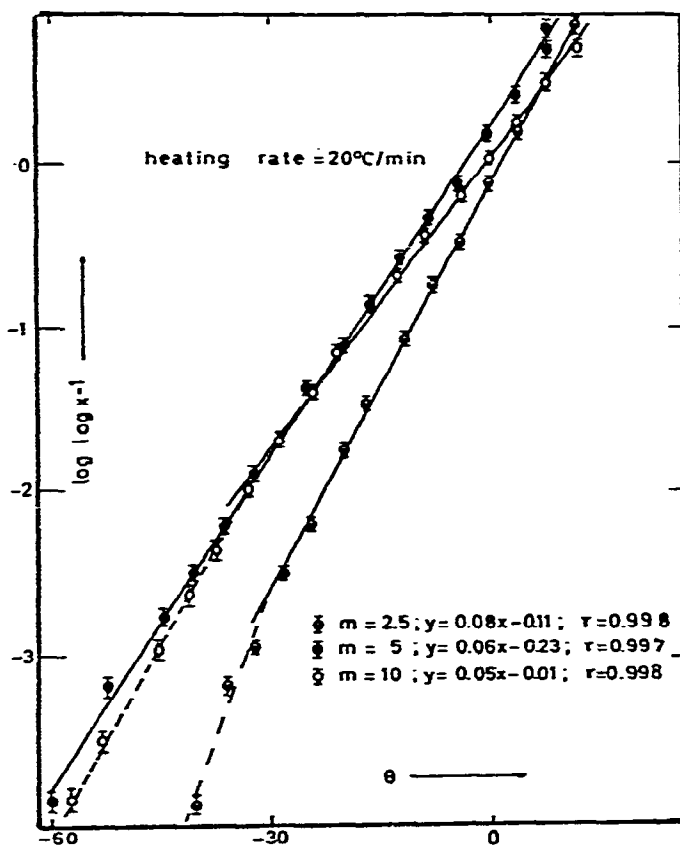

Fig. 1. Experimental plot of the D–K method.

120

The other method used was the differental of F–C[11]. A typical plot of this method is shown in Fig. 2.
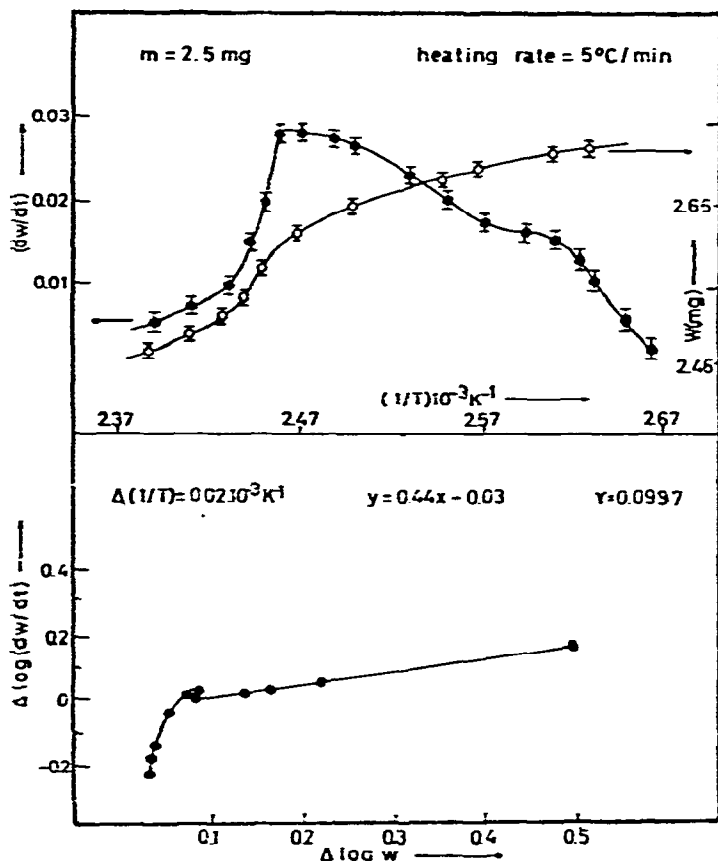

Fig. 2. Experimental plot of the F–C method.

Table 2 shows the activation energies as well as reaction order parameters obtained from both D–K and F–C methods. The values obtained in other works are also shown in the same table for comparison.

The use of a small mass shows a lower deviation of the average values in relation with those obtained using a large mass. Consequently by using a small mass a more correct experimental agreement with suppositions of the theoretical treatment about the diffusion phenomena and temperature gradient in the sample is obtained.

This interpretation can be confirmed by the fact that a great dependence of the activation energy and order parameter on the heating rate was not observed when we use a large interval.

Also it should be noted that the differential method of F–C presents a lower approximation than the D–K method (a higher dispersion of values for activation energy was obtained).

TABLE 2

ACTIVATION ENERGIES AND ORDER PARAMETERS AS A FUNCTION OF THE MASS OF THE SAMPLE AND HEATING RATE

Heating rate (°C min^{-1})	Mass (mg)	n	E_a (kcal mol^{-1})
Horowitz–Metzger/Dharwadkar–Karkhanavala integral method			
1.25	2.50	1/2 − 1	12.5
	5	1	13.3
	10	1	12.2
5	2.50	1 − 3/2	13.4
	5	1	13.2
	10	1	14.6
20	2.50	1/2 − 1	15.6
	5	1	15.2
	10	1	15.0
80	2.50	1/2 − 1	15.0
	5	1	15.5
	10	1	16.1
Freeman–Carroll differential method			
$(1/T)$ = cst.	2.50	1/2	8.2
5	10	1	10.3
$(1/T) \neq$ cst.	2.50	3/4	11.3
5	10	1/2 − 1	15.6

Mass (mg)	Activation energy (kcal mol^{-1})		
Heating rate (°C min^{-1})	2	4	8
Dharwadkhar–Karkhanavala[9] with n = 1			
162	16.5	18.2	17.7
405	18.9	18.2	17.7
648	19.6	20.0	21.2
1215	19.5	21.0	20.6
1782	21.3	—	20.8
2430	21.0	—	20.4
Dharwadkhar–Karkhanavala/Coats–Redfern with n not defined[9]			
Heating rate (°C min^{-1})	1	5	10
70	20.7	21.7	22.9
200	25.3	23.9	24.6
300	24.3	20.5	22.4

REFERENCES

1 J. Šesták, V. Šatava and W. W. Wendlandt, *Thermochim. Acta*, 5 (1973) 335.
2 D. A. Young, *Decomposition of Solids*, Pergamon Press, New York, 1966.
3 V. P. Auffredic and P. Vallet, *C.R. Acad. Sci.*, 236C (1966) 652.

4 M. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, Clarendon Press, London, 1959.
5 A. Richer, *Publ. Inst. Rech. Siderurg.*, Ser. A, 187 (1960).
6 P. Vallet and A. Richer, *C.R. Acad. Sci.*, 238C (1954) 1020.
7 A. E. Newkirk, *Ancl. Chem.*, 32 (1960) 1558.
8 D. Bidard-Vigouroux, *Doctoral Thesis*, Rennes 1969.
9 Dharwadkar and Karkhanavala, *Thermal Analysis*, Vol. 2, Elsevier, New York, 1969.
10 H. H. Horowitz and G. Metzger, *Anal. Chem.*, 35 (1963) 1464.
11 E. S. Freeman and B. Carroll, *J. Phys. Chem.*, 62 (1958) 394.
12 E. H. Bocanegra, J. J. Icaza, M. J. Tello and H. Arend, to be published, *4th Int. Conf. Chem. Thermodyn., Montpellier, 1975*.
13 J. Simon, *J. Therm. Anal.*, 5 (1973) 271.