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Note

CHARACTERISTIC KINETIC PARAMETERS IN SOLID → SOLID + GAS REACTIONS. COMPENSATION EFFECTS

M.R. ALVAREZ, M.J. TELLO and E.H. BOCANEGRA

Departamento de Física, Facultad de Ciencias, Universidad del País Vasco, Bilbao (Spain)

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The influence of experimental factors on thermogravimetric results using both dynamic and isothermal or quasi-isothermal methods has been extensively studied in the last few years (see for example ref. 1 and refs. cited therein). The interest in this kind of study is to acquire enough experimental data under very well-defined conditions to establish a general experimental procedure as well as a theoretical methodology [2,3].

Two characteristic parameters are especially influenced by experimental conditions: the activation energy and the pre-exponential factor [4]. For instance, the values found in the literature for the activation energy and pre-exponential factor of CO_3Ca range from 37 to 377 kcal $mole^{-1}$ and 10^2—10^{68}, respectively. Zsákó [5] observed an interesting dependence between both magnitudes, and explained it as arising from a "compensation" effect in the sense that an increase in the activation energy implies an increase in the probability of nucleation.

The purpose of this paper is to present a detailed study on the existence of this compensation effect in a solid → solid + gas reaction. We show that this effect is common to dynamic as well as isothermal procedures, in contrast to previously reported studies [6].

EXPERIMENTAL

$(CH_3NH_3)_2MnCl_4$ was the compound used throughout the study [7]. The reason for this choice was to study a material more complex than those previously studied (i.e. calcium carbonate or calcium oxalate). Problems related to the synthesis, characterization, as well as thermal stability, have been published previously [7]. In the present study our analysis is restricted to the first step of the decomposition process [7]. Experimental details about experimental equipment as well as calibration and working conditions can be seen in refs. 2 and 15. In order to check the possible influence on the results of the instrument used, TG measurements were also carried out using a Dupont thermobalance with simultaneous TG and DTG.

The experimental conditions were: dynamic, dry N_2 atmosphere at 25 ml min^{-1}, a constant sample mass of 5 mg for all the experimental runs, and heating rates of 2,5; 5; 5,5; 10 and 20°C min^{-1} for dynamic runs and for the isothermal regime 463; 473; 483 and 493 K, respectively.

TABLE 1

Values of kinetic parameters from different theoretical methods

V_c (°C min^{-1})	Kinetic parameter	Dynamic regime					
		Integral methods			Misc. Method	Other methods	
		Ref. 8	Ref. 9	Ref. 10	Max. point (ref. 11)	Ref. 12	Ref. 13
2.5	E *	16.70	15.00	27.50	16.61	16.65	20.67
	n	0.75	0.75		0.75	0.22	0.58
	A **	9.60×10^5	1.60×10^5	4.87×10^9	8.70×10^5	7.0×10^5	60×10^7
5	E *	26.60	21.78	35	23.51	28.97	19.91
	n	0.46	0.46		0.46	1.60	0.30
	A **	1.60×10^{10}	1.43×10^8	1.97×10^{11}	7.80×10^8	2.56×10^{11}	1.82×10^6
10	E *	27.89	20.65	42.50	26.04	40.68	13.85
	n	0.58	0.58		0.58	2.22	-0.14
	A **	4.50×10^{10}	4.60×10^8	4.38×10^{15}	7.80×10^9	1.76×10^{16}	1.78×10^4
20	E *	35.18	27.35	52.50	32.35	41.56	31.17
	n	0.46	0.46		0.46	1.76	0.39
	A **	7.53×10^{12}	8.86×10^9	6.85×10^{18}	6.46×10^{11}	7.31×10^{15}	3.70×10^{11}

V_c (°C min^{-1})	Kinetic parameter	Isothermal regime			Multiple heating rate (ref. 14)		
		Integral methods		Other method	x		
		Ref. 8	Ref. 10	Simple law	0.46	0.70	0.90
2.5	E *	14.33	20.47	18.44			
	n	0.15		0.15			
	A **	2.8×10^4	1.4×10^7	5.6×10^2			
5	E *						
	n						
	A **						
10	E *				19.30	21.47	19.07
	n				5.78	5.78	0.17
	A **				7.28×10^8	8.83×10^6	4.28×10^6
20	E *						
	n						
	A **						

* kcal mole^{-1}.
** min^{-1}.

TABLE 2

Values of kinetic parameters from different theoretical methods

V_c (°C min^{-1})	Kinetic parameter	Dynamic regime					
		Horowitz–Metzger	Coats–Redfern	Satava (Geom.)	Max. point	Freeman–Carroll	Ratio
5.5	E *	18.19	15.05	30	18.93	30.20	20.77
	n	0.45	0.45		0.45	4.15	0.61
	A **	3.25×10^7	1.04×10^6	1.66×10^{12}	2.6×10^8	4.74×10^{13}	4.60×10^8

* kcal mole^{-1}.

** min^{-1}.

RESULTS AND DISCUSSION

Tables 1 and 2 show the kinetic data for each theoretical analysis method. From Table 1 we can see how E increases with V_c which is in agreement with our previous results for calcium oxalate [2]. This can be explained using Kissinger's correlation [16] which can be written

$$\ln\left(\frac{V_c}{CT_{max}^2}\right) = -\frac{E}{RT_{max}} \tag{1}$$

where values of C lie between 2×10^2 and 10^8 and T_{max} is the temperature at the point of maximum reaction rate which shows a linear dependence with V_c given by

$$T_{max} = 508 + 3.8V_c \tag{2}$$

It can be seen (Table 1) that a similar relationship to the one between E and V_c also exists for log A. Figure 1 is a plot of $\log A$ vs. E for both dynamic and isothermal data from Table 1 fitting a straight line given by

$$\log A = -0.41 + 0.38E \tag{3}$$

The same type of correlation was found for the Dupont thermobalance as shown in Fig. 2 (Table 2).

This correlation between A and E (compensation effect) can be derived from the Arrhenius equation [17,18]

$$A = Z \exp\left(\frac{\Delta S^*}{R}\right) \tag{4}$$

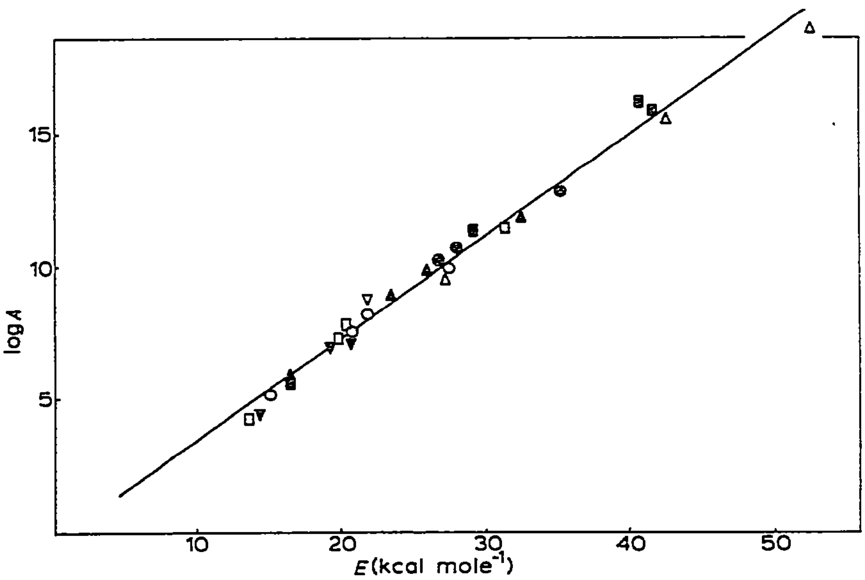

Fig. 1. Compensation effect from data in Table 1. $\log A = 0.385E - 0.413$; $r^2 = 0.985$. ●, Horrowitz—Metzger; ○, Coats—Redfern; △, Satava (geometrical); ▲, maximum point; ■, Freeman—Carroll; □, ratio; ▽, Friedman; ▼, isothermal.

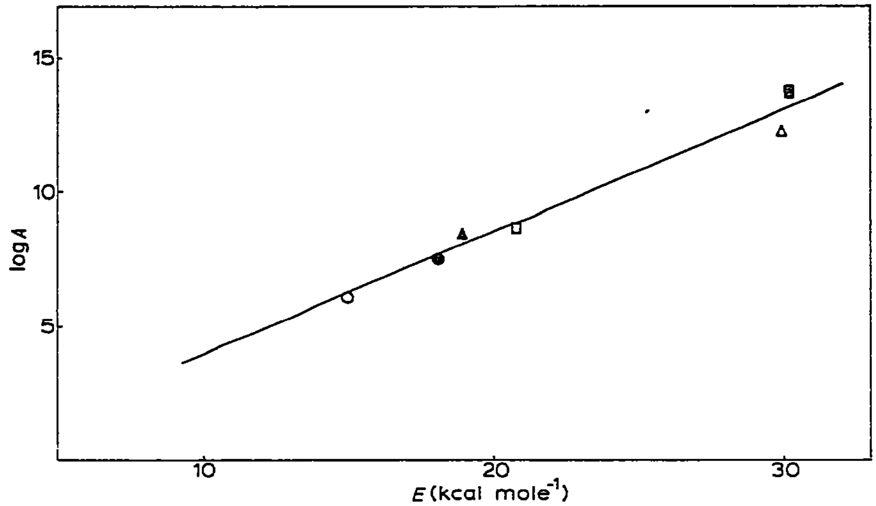

Fig. 2. Compensation effect from data in Table 2. $\log A = 0.451E - 0.592$; $r^2 = 0.972$. ●, Horowitz—Metzger; ○, Coats—Redfern; △, Satava (graphical); ▲, maximum point; ■, Freeman—Carroll; □, ratio.

where ΔS^* is the entropy variation of the activated complex and as

$$d(\Delta S^*) = \frac{1}{T} d(\Delta H^*) \tag{5}$$

it follows

$$\frac{d(\log A)}{dE} = \frac{\log e}{RT_m} \tag{6}$$

where $\Delta H^* \simeq E$ and T_m is a characteristic parameter for each compound (564 K in our case). The invariance of this parameter under several theoretical methods and experimental conditions should be emphasized.

The experimental results in this paper have confirmed the existence of a logarithmic correlation between the activation energy, E, and the pre-exponential factor, A. Nevertheless, more experimental work with other compounds is required to confirm the general character of the characteristic parameter, T_m. At present a similar study on other possible invariant characteristics of kinetic parameters [19] is being carried out in our laboratory.

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