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Note

THE METHOD OF CALCULATION OF KINETIC PARAMETERS AS A POSSIBLE CAUSE OF APPARENT COMPENSATION EFFECTS

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INTRODUCTION

The study of the significance of the compensation effect between the logarithm of the Arrhenius pre-exponential factor and the activation energy of heterogeneous reactions has received a great deal of attention [1—6]. Recent papers [7—11] have shown that very often the compensation effects reported in the literature are rather apparent and motivated by the influence of secondary effects on the reactions that leads to apparent kinetic parameters. The experimental errors, the effect of the particle size distribution and the heat and mass transfer phenomena have been considered as the major causes leading to the observation of an apparent compensation effect [12].

However, little, if any, attention has been paid to the study of whether the use of different methods of calculation for obtaining the kinetic parameters of one and the same reaction would be a possible source of apparent compensation effects. We think that this study merits attention after considering that compensation effects between the kinetic parameters obtained by different authors for the same reaction have been reported in several reviews [6,13]. Moreover, chemical interpretations of the phenomenon have been given in spite of the fact that the assumed reaction mechanism has not always been the same.

The scope of the present paper is to explore the influence of both the method of calculation and the kinetic law assumed for performing the analysis of single TG—DTG traces of $CdCO_3$, $MnCO_3$ and $PbCO_3$ on their kinetic parameters in order to determine if they are correlated through a compensation effect.

EXPERIMENTAL

$CdCO_3$, $MnCO_3$ and $PbCO_3$, d'Hemio AR were used. The TG and DTG curves were obtained simultaneously under a vacuum of 10^{-4} torr using a

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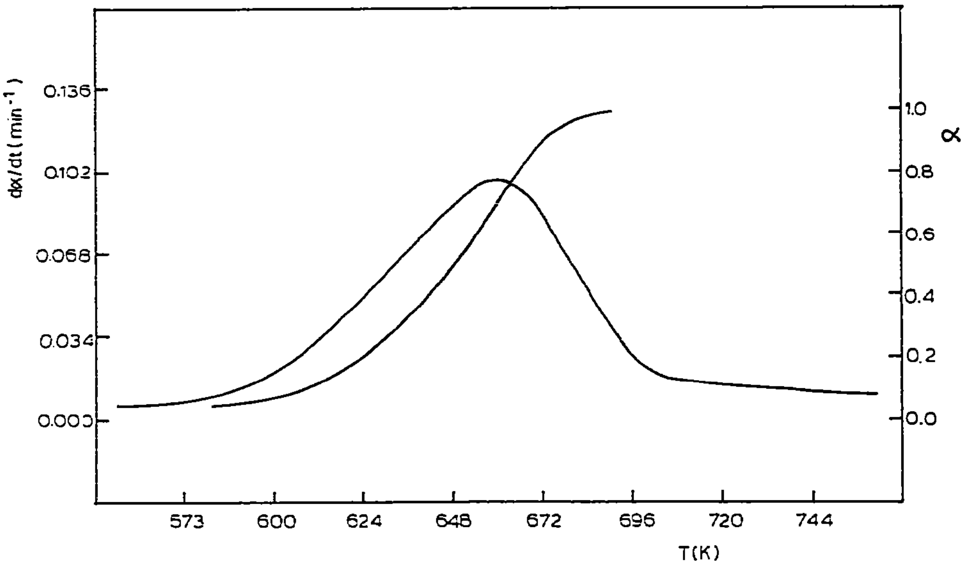

Fig. 1. TG and DTG curves of the thermal decomposition of $CdCO_3$.

Cahn electrobalance, model RG, equipped with a derivatograph Mark II. Sample weights of about 23 mg and a heating rate of 6°C min^{-1} were used.

RESULTS AND DISCUSSION

The TG and DTG curves of the thermal decomposition of $CdCO_3$, $MnCO_3$ and $PbCO_3$ are included in Figs. 1, 2 and 3, respectively. Kinetic analysis of

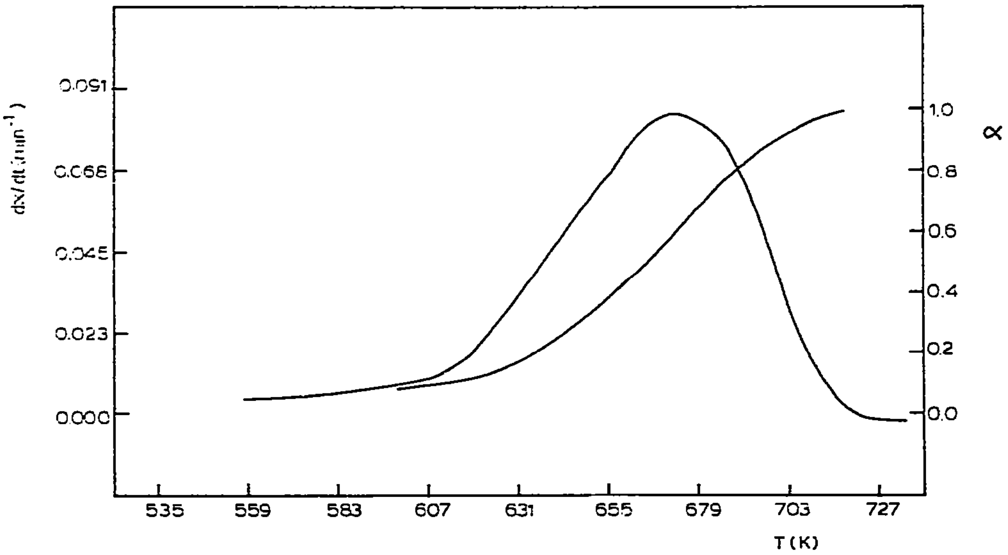

Fig. 2. TG and DTG curves of the thermal decomposition of $MnCO_3$.

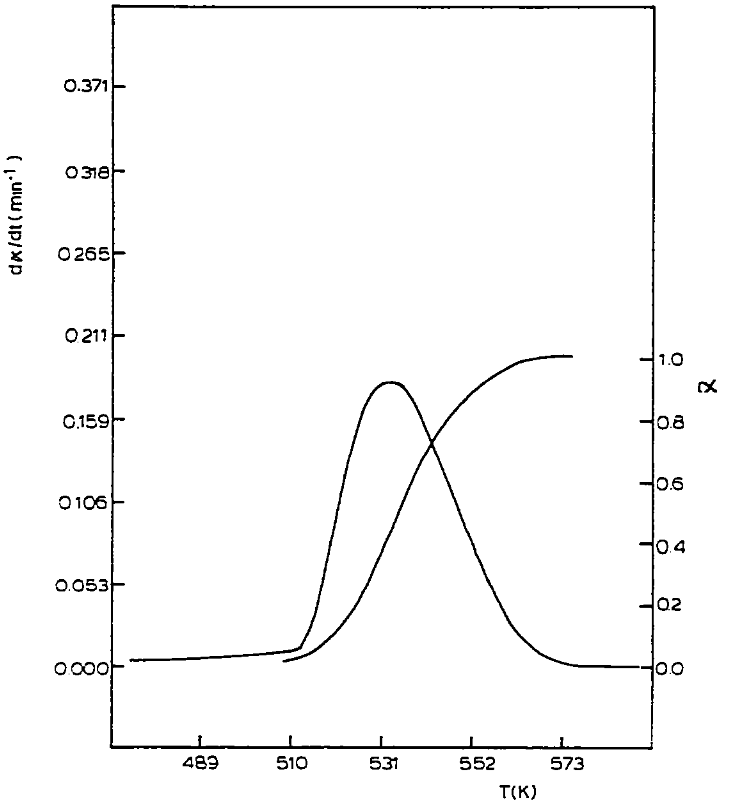

Fig. 3. TG and DTG curves of the thermal decomposition of $PbCO_3$.

the above data has been carried out by means of the Coats and Redfern [14] method

$$\ln g(\alpha) - 2 \ln T = \ln \frac{AR}{E\beta} \times \frac{E}{RT} \tag{1}$$

and that of Achar et al. [15]

$$\ln \frac{(d\alpha/dt)}{f(\alpha)} = \ln A - \frac{E}{RT} \tag{2}$$

where α is the reacted fraction at time t, β is the heating rate, E is the activation energy, A is the Arrhenius pre-exponential factor and $f(\alpha)$ and $g(\alpha)$ are mathematical functions depending on the reaction mechanism.

When the functions $f(\alpha)$ and $g(\alpha)$ fit the experimental data, plots of the left-hand side of eqns. (1) and (2) against the reciprocal of the absolute temperature give straight lines whose slopes and intercepts yield the apparent activation energy and the apparent Arrhenius pre-exponential factor, respctively.

The results obtained from kinetic analysis of the data included in Figs. 1—3, by taking into account the $f(\alpha)$ and $g(\alpha)$ functions corresponding to the mechanisms more commonly used in the literature for describing the thermal decomposition of solids, are included in Tables 1—3. We can see that the experimental data fit most of the kinetic equations tested.

TABLE 1

Kinetic parameters obtained from analysis of the curves in Fig. 1 by different methods of calculation and different kinetic laws

Mechanism	Integral method			Differential method		
	E(kcal mole^{-1})	A(min^{-1})	Regression coefficients	E(kcal mole^{-1})	A(min^{-1})	Regression coefficients
R_1	25.2	2.7×10^7	-0.99678	9.5	1.2×10^2	-0.89177
R_2	31.9	7.0×10^9	-0.99957	26.8	1.3×10^8	-0.99951
R_3	34.4	5.6×10^{10}	-0.99974	32.6	1.3×10^{10}	-0.99885
$F_1(\alpha)$	39.8	5.1×10^{12}	-0.99912	44.2	1.3×10^{14}	-0.99493
A_2	37.3	4.3×10^{10}	-0.99902	45.9	2.9×10^{13}	-0.98694
A_3	34.7	1.8×10^8	-0.99888	47.6	4.1×10^{12}	-0.97631
D_1	53.0	6.2×10^{16}	-0.99712	37.3	2.8×10^{11}	-0.98427
D_2	61.1	2.4×10^{19}	-0.99902	52.0	1.7×10^{16}	-0.99779
D_3	71.3	2.2×10^{22}	-0.99976	69.6	4.7×10^{21}	-0.99964
D_4	64.5	8.4×10^{19}	-0.99946	58.0	1.1×10^{18}	-0.99942

Figures 4—6 show that plots of the logarithms of Arrhenius pre-exponential factor vs. the corresponding values of the activation energy lead to compensation effects represented by the equations quoted in Table 4.

The above results show that the differences in the kinetic parameters reported for a reaction would be motivated by both the method of calculation used and/or the kinetic law previously assumed. Moreover, in such a case ln A and E seem to be connected through a compensation effect.

TABLE 2

Kinetic parameters obtained from analysis of the curves in Fig. 2 by different methods of calculation and different kinetic laws

Mechanism	Integral method			Differential method		
	E(kcal mole^{-1})	A(min^{-1})	Regression coefficients	E(kcal mole^{-1})	A(min^{-1})	Regression coefficients
R_1	19.7	2.0×10^5	-0.99420	7.8	2.8×10^1	-0.85459
R_2	23.9	7.0×10^6	-0.99758	18.3	1.1×10^5	-0.99258
R_3	25.5	2.6×10^7	-0.99813	21.7	1.8×10^6	-0.99751
$F_1(\alpha)$	28.8	4.1×10^8	-0.99847	28.7	4.7×10^8	-0.99887
A_2	26.2	2.3×10^6	-0.99816	25.9	3.5×10^6	-0.99777
A_3	23.6	6.1×10^3	-0.99774	23.2	1.6×10^4	-0.99452
D_1	42.1	4.7×10^{12}	-0.99495	30.2	6.1×10^8	-0.97663
D_2	47.3	1.7×10^{14}	-0.99699	39.3	4.3×10^{11}	-0.99247
D_3	53.6	6.5×10^{15}	-0.99832	49.9	4.4×10^{14}	-0.99835
D_4	49.4	2.1×10^{14}	-0.99759	42.9	3.9×10^{12}	-0.99558

TABLE 3

Kinetic parameters obtained from analysis of the curves in Fig. 3 by different methods of calculation and different kinetic laws

Mechanism	Integral method			Differential method		
	E(kcal mole^{-1})	A(min^{-1})	Regression coefficients	E(kcal mole^{-1})	A(min^{-1})	Regression coefficients
R_1	33.5	8.0×10^{12}	−0.98458	−9.6	2.0×10^{-5}	−0.83812
R_2	41.3	1.8×10^{16}	−0.99029	10.1	3.2×10^{3}	−0.92843
R_3	44.2	3.1×10^{17}	−0.99166	16.6	1.7×10^{6}	−0.97651
$F_1(\alpha)$	50.4	1.4×10^{20}	−0.99372	29.7	5.0×10^{11}	−0.99155
A_2	48.3	2.3×10^{18}	−0.99314	6.9	3.2×10^{1}	−0.87509
A_3	46.2	2.1×10^{16}	−0.99249	−15.9	1.2×10^{-9}	−0.94398
D_1	69.1	2.8×10^{27}	−0.98551	26.0	6.8×10^{9}	−0.91167
D_2	78.7	1.6×10^{31}	−0.98898	42.9	4.0×10^{16}	−0.97126
D_3	90.5	3.5×10^{35}	−0.99205	62.9	1.9×10^{24}	−0.98922
D_4	82.6	1.6×10^{32}	−0.99018	49.8	1.4×10^{19}	−0.98057

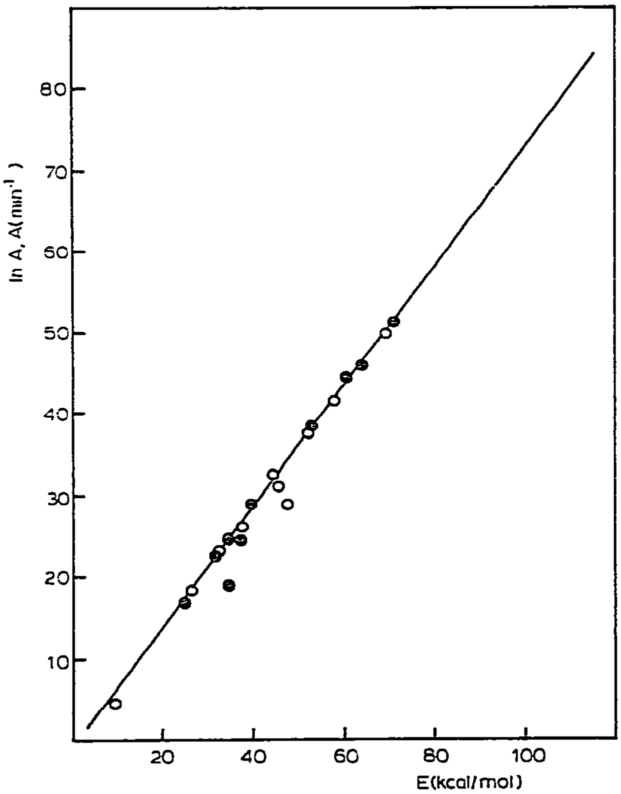

Fig. 4. Compensation effect between the kinetic parameters quoted in Table 1 for the thermal decomposition of $CdCO_3$. ○, Differential method; ●, integral method.

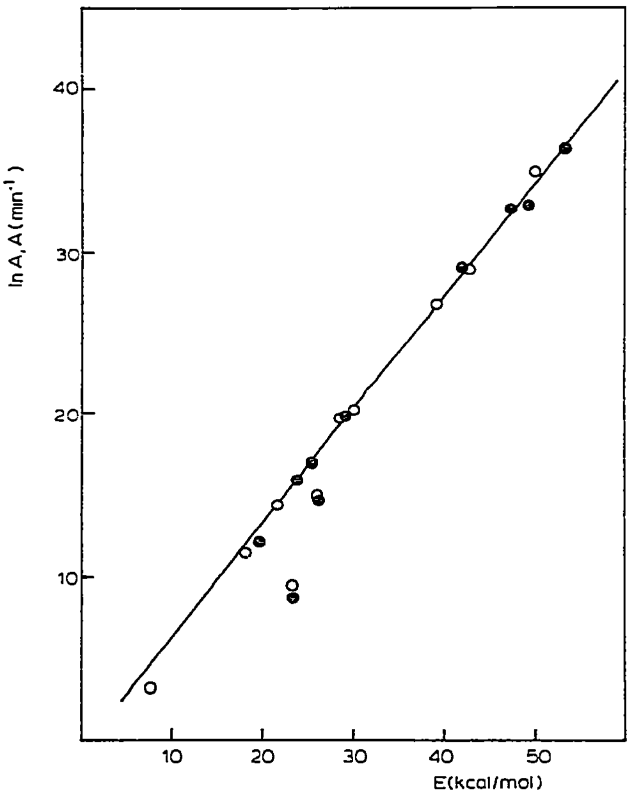

Fig. 5. Compensation effect between the kinetic parameters quoted in Table 2 for the thermal decomposition of $MnCO_3$. ○, Differential method; ●, integral method.

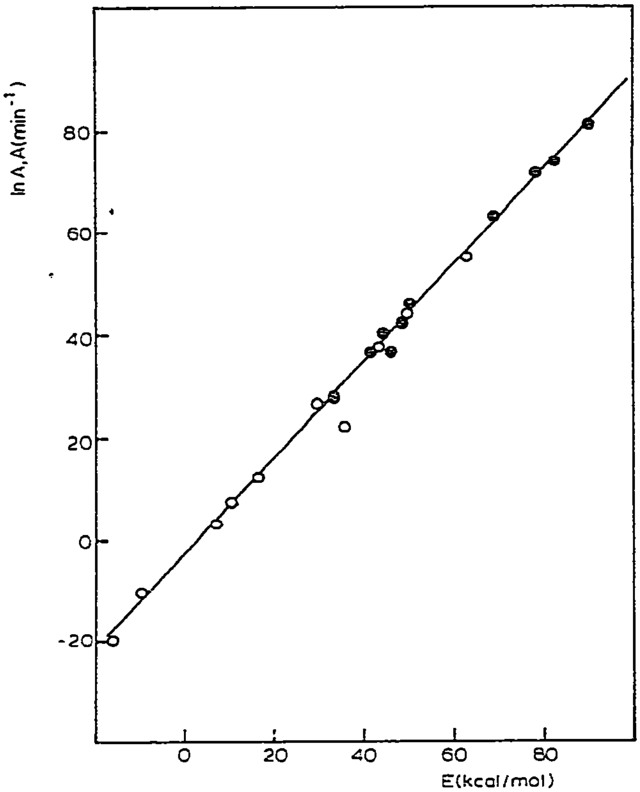

Fig. 6. Compensation effect between the kinetic parameters quoted in Table 3 for the thermal decomposition of $PbCO_3$. ○, Differential method; ●, integral method.

TABLE 4

Mathematical expressions of the compensation effect

Sample	Equation
$CdCO_3$	$\ln A = 0.75E - 2.30$
$MnCO_3$	$\ln A = 0.76E - 3.81$
$PbCO_3$	$\ln A = 0.92E - 1.56$

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