

EXPERIMENTAL STUDY OF NON-ISOTHERMAL KINETIC EQUATIONS AND COMPENSATION EFFECT

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What science does, in fact, is to select the simplest formula that will fit the facts...If the simplest formula ceases, after a time, to be applicable, the simplest formula that remains applicable is selected, and science has no sense that an axiom has been falsified.

B. Russell [1]

ABSTRACT

The relation of kinetic constants calculated by various differential equations was studied using calcium carbonate as a model substance. Strict correlation has been found between the kinetic constants (A, E, n, m, p), indicating a very formal character and the practical equivalency of the various differential equations used for evaluation of the thermoanalytical curves. This is an important reason for the kinetic compensation effect, C.E. (i.e., the linear $\ln A$ vs. E function), which exists in the cases of heterogeneous, homogeneous, isothermal and non-isothermal examinations alike, enhancing the complexity of the mechanism of the different thermal processes. Correlations similar to the C.E. have also been revealed between the coefficients of a sixth order polynomial fitted to the measured DTG curves.

Exploiting the formal character of the usual differential equations, the idea of the compensation effect of a single measurement (C.E.), can be introduced using three or four various differential equations for the calculation of the kinetic constants. This affords the quantitative examination of the effect of the measuring circumstances on the mechanism of the investigated thermal process.

INTRODUCTION

Besides the analytical use of thermoanalytical investigations and the attempts to obtain a kinetic analysis from the data, a third tendency can be ascertained, namely to obtain information which can be of direct use in technological problems. In this respect the requirement is the practical characterization of the behaviour of the material within specified practical circumstances, physical processes and chemical mechanisms. There are, however, problems inherent in the technique of thermal analysis which could hinder its use in solving technological problems.

In the last decades an immense amount of work has been carried out to solve these problems of thermal analysis and its application has been extended to new domains. These widespread thermoanalytical efforts have furnished enough data for Šestak [2] to present a general and theoretical review on the subject. Independent of this it can be stated that the development of thermal analysis has been determined by the principle of seeking constants characteristic of the reactions undergone by the examined substance. It is a well known fact, however, that the measured data, namely the peak temperature and the calculated results (i.e., the kinetic constants), are the functions of the measuring circumstances, the sample mass, the particle size, the packing, "inert" additives, the heating rate, the shape and the material of the sample holder, the atmosphere, etc. It is a natural consequence that *the "elimination" of the effects of the measuring circumstances has become an important task instead of the determination of their effects.*

This is just one of the important reasons for the very comprehensive studies which have been reported on the development of methods and equations—mainly based on the Arrhenius equation—which would describe the processes [3–15]. Numerous models have been suggested in the literature and methods were developed to look for the differential equation which could represent the measured data with the greatest proximity (e.g., refs. 4, 13, 16–21).

This was the method used by Fong and Chen [22], which is chosen here as an example. They looked for the best solution to represent the decomposition of magnesium hydroxide and they used in the trial-and-error procedure the 17 differential equations shown in Table I taken from the publication by Gallagher and Johnson [23]. This procedure became particularly important because the non-isothermal measurements appeared to be a more simple approach to investigate kinetic parameters and gave much more data in comparison with the roundabout and lengthy isothermal measurements (e.g., refs. 17, 18, 21).

Although many measuring methods and equations have been recommended to characterize the thermal processes (e.g., decomposition), the comparison of the thermal analysis curves and the calculation of data has not been completely possible in spite of the far-reaching investigations of measuring circumstances (e.g., refs. 3–6, 24) errors and accuracy (e.g., refs. 3, 7).

Some problems "could be shoved under the carpet" [25] by very sensible (or sophisticated?) and very expensive instruments, but the problem of comparing data measured under different circumstances remains open. The problem of description is obviously unsolved too. This is evident from critical, sceptical or even ironical opinions (e.g., refs. 25–29).

An important result of the kinetic research is the observation of the kinetic compensation effect, C.E., namely the linear relationship between the logarithm of the pre-exponential factors and the activation energies. The

TABLE 1

Kinetic functions suggested for the trial-and-error procedure

$$g(\alpha) = \int_0^\alpha d\alpha / f(\alpha)$$

	$g(\alpha)$	$f(\alpha)$	Mechanism
1	α	α^0	Power law
2	α^2	α^{-1}	
3	$\alpha^{1/2}$	$\alpha^{1/2}$	
4	$\alpha^{1/3}$	$\alpha^{2/3}$	
5	$\alpha^{1/4}$	$\alpha^{3/4}$	
6	$1 - (1 - \alpha)^{1/2}$	$(1 - \alpha)^{1/2}$	Contracting geometry
7	$1 - (1 - \alpha)^{1/3}$	$(1 - \alpha)^{2/3}$	
8	$-\ln(1 - \alpha)$	$(1 - \alpha)$	
9	$[-\ln(1 - \alpha)]^{1/1.5}$	$(1 - \alpha)[- \ln(1 - \alpha)]^{1/3}$	Erofeev
10	$[-\ln(1 - \alpha)]^{1/2}$	$(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$	
11	$[-\ln(1 - \alpha)]^{1/3}$	$(1 - \alpha)[- \ln(1 - \alpha)]^{2/3}$	
12	$[-\ln(1 - \alpha)]^{1/4}$	$(1 - \alpha)[- \ln(1 - \alpha)]^{3/4}$	
13	$\alpha + (1 - \alpha) \ln(1 - \alpha)$	$[-\ln(1 - \alpha)]^{-1}$	Diffusion controlled, 2D
14	$1 - 2\alpha/3 - (1 - \alpha)^{2/3}$	$[-\ln(1 - \alpha)]^{-1}$	Diffusion controlled, 3D
15	$[1 - (1 - \alpha)^{1/3}]^2$	$(1 - \alpha)^{1/3} - \ln(1 - \alpha)^{-1}$	Jander
16	$(1 - \alpha)^{-1} - 1$	$(1 - \alpha)^2$	Second order
17	$(1 - \alpha)^{-1/2} - 1$	$(1 - \alpha)^{1.5}$	One and a half order

C.E. can be observed in many cases of heterogeneous reactions. The idea of regarding the C.E. as a consequence of the errors of measurements or as an imperfection of the Arrhenius equation has never occurred for the homogeneous phase, especially for isothermal measurements, so these could be the norms of the ironic criticism of the measurements in the heterogeneous phase. According to Garn [27], for example, "The Arrhenius equation is widely used in heterogeneous kinetics for two reasons. First, the relationship is well established in homogeneous kinetics; second, the form of the equation assures the user that number for the constants in the equation can be calculated..." In accordance with this remark, it would seem better to give up the use of the Arrhenius equation applied to heterogeneous phase reactions. However, according to Garn again [27], the C.E. can give some information about mechanism and is not just a formal relationship, because "From examination of the general nature of the "kinetic compensation effect", it appears that the reactions involved in these examples have a feature in common—a principal reaction in which some parameter changes the temperature variation without changing the general nature of the reaction... the C.E. may be instructive in deducing the nature of the temperature dependence."

The basis of such and similar contradictions is the fact that the mechanisms of thermal reactions are equally complicated in homogeneous, heterogeneous, isotherm and non-isotherm examinations. The C.E. is closely related to the description of the thermal processes and it was noted a long time ago both in homogeneous phase and in heterogeneous catalytic reactions. Cremer [30] attributed the C.E. to two sources, namely the unidirectional change of entropy, and enthalpy of activation of superimposed part processes and experimental errors; however, these can hardly explain the linearity of the C.E. reassuringly.

The C.E. is also noticeable in thermoanalytical data because of the greatly extended kinetic analysis of the measured curves [31,32], but this was only recently realized (e.g., refs. 33-37) and is often not commented upon at all (e.g., refs. 17, 18, 38, 39).

From these facts and opinions it was decided in the present study to examine how the various equations on the basis of the Arrhenius relationship can express the superimposition of part-processes and can be related by a compensation effect and by the experimental conditions including industrial experience.

EXPERIMENTAL AND METHODS

Calcium carbonate was chosen as a model substance because much of the data available regarding its decomposition and the products of decomposition are well defined and used in various industrial processes, e.g., lime kilning, production of cement, desulphurization of flue gases, etc.

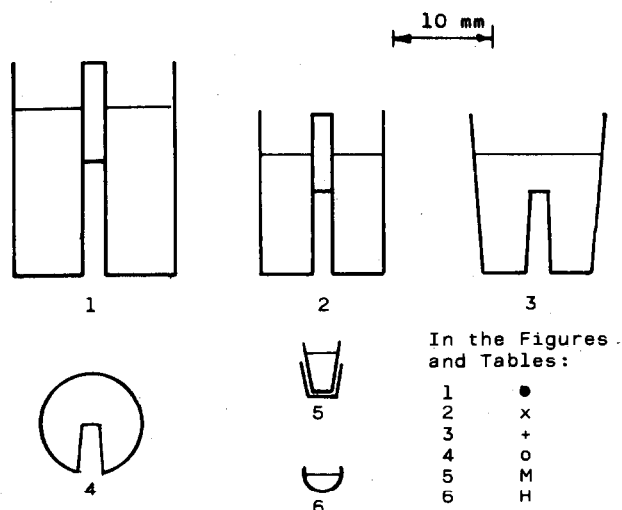


Fig. 1. The shapes of the samples.

The sample mass and the heating rate ranged from 0.8 to 3460 mg and from 3 to 13 K min⁻¹, respectively. The shape of the sample (Fig. 1) and the type of balance (Derivatograph, Heraeus TGA-500, Mettler)* were also varied.

The following differential equations suggested by Šestak [8] on a theoretical basis were used for the evaluation of the decomposition data of the calcium carbonate

$$-d\alpha/dt = A \exp(-E/RT)(1-\alpha)^n \quad (1)$$

$$-d\alpha/dt = A \exp(-E/RT)(1-\alpha)^n \alpha^m \quad (2)$$

$$-d\alpha/dt = A \exp(-E/RT)(1-\alpha)^n [-\ln(1-\alpha)]^p \quad (3)$$

$$-d\alpha/dt = A \exp(-E/RT)(1-\alpha)^n \alpha^m [-\ln(1-\alpha)]^p \quad (4)$$

where $-d\alpha/dt$ is the rate of decomposition; $(1-\alpha)$ is the reaction coordinate; A is the pre-exponential factor; E is the activation energy; R is the gas constant; T is the absolute temperature; and n , m and p are orders of the reaction.

According to the suppositions, these equations express the thermal decomposition, its reversibility, the nucleation, the diffusion and the combination of these processes [8], which are obviously important in the case of calcium carbonate.

RESULTS AND DISCUSSION

The C.E. in the case of various equations

The data measured in sample holder 1 (Fig. 1) with a heating rate of 9 K min⁻¹ can be seen in Table 2. Using very different measuring conditions the calculated data have been collected in Table 3.

The C.E. is also observed in this case. In addition to this, the results make it possible to show the existence of the C.E. even in the parameter range where the separate kinetic constants cannot have any direct physical meaning.

Another important fact is that the C.E. connects different kinetic models [40,41]. As an example, Fig. 2 shows the data for runs using 200 mg and 2000 mg samples given in Table 2. It is noted in part B of Table 2 how strict the correlation is among the "kinetic constants" calculated using four differential equations. It is obvious from Tables 2 and 3 that not the kinetic

* Certain commercial equipment is identified in this paper in order to specify adequately the experimental procedure. In no case does identification imply recommendation or endorsement by the authors, nor does it necessarily imply the equipment identified is necessarily the best available for the purpose.

TABLE 2
Variation in kinetic parameters (calculated using different equations)

<i>Part A</i>					
Sample mass (mg)	100	200	400	1000	2000
Temp. (°C)	680–820	670–840	680–850	740–905	830–908
ln <i>A</i>	19.69	19.36	17.55	16.25	20.69
<i>E</i> (kJ mole ⁻¹)	229.91	226.85	217.77	213.79	260.22
<i>n</i>	0.45	0.38	0.39	0.41	0.52
<i>r</i> eqn. (1)	0.9986	0.9953	0.9979	0.9980	0.9937
ln <i>A</i>	138.95	-13.20	41.71	-5.80	-6.43
<i>E</i> (kJ mole ⁻¹)	1282.35	-68.67	446.33	0.14	-3.56
<i>n</i>	1.35	0.19	0.40	0.32	0.34
<i>m</i>	-4.25	1.28	-1.22	0.97	0.91
<i>r</i> eqn. (2)	0.9994	0.9969	0.9982	0.9990	0.9967
ln <i>A</i>	83.95	-29.87	39.05	18.23	-0.20
<i>E</i> (kJ mole ⁻¹)	795.95	-217.31	420.71	232.80	57.74
<i>n</i>	0.03	0.75	-0.04	0.39	0.62
<i>p</i>	-2.24	1.86	-1.07	-0.09	0.66
<i>r</i> eqn. (3)	0.9990	0.9975	0.9982	0.9980	0.9955
ln <i>A</i>	141.32	-30.34	41.36	-1.16	-2.25
<i>E</i> (kJ mole ⁻¹)	1303.92	-218.98	442.82	41.62	32.28
<i>n</i>	1.95	0.79	0.17	-0.74	-1.15
<i>m</i>	-5.79	-0.11	-0.65	3.95	5.17
<i>p</i>	1.43	2.00	-0.54	-3.00	-4.14
<i>r</i> eqn. (4)	0.9994	0.9998	0.9982	0.9996	0.9985
<i>Part B</i>					
	$\ln A = a_0 E + a_1$				
<i>a</i> ₁	-6.3020	-5.7839	-5.4843	-5.6422	-5.9071
<i>a</i> ₀	0.1133	0.1112	0.1058	0.1026	0.1022
<i>r</i>	1.0000	0.9999	1.0000	0.9999	0.9998

constants but the slope of the C.E. plot can be related to the change of the sample mass and other parameters.

Although there is an extreme variation in values of the kinetic constants the fitness of the description is very remarkable and practically independent of the type of differential equation used [40,41]. Similar results were found by Criado and Gonzales [42] for CdCO₃, MnCO₃ and PbCO₃, verifying Várhegyi's [15] opinion that "if the number of parameters is too large, different sets of values of the parameters can provide an acceptable fit between the experimental data and the corresponding theoretical data". In agreement with results of Guarini et al. [43], *it is obvious that numerous different kinetic equations give linear or semilinear Arrhenius plots with similar fit and as a result the selection of the rate determining process seems to be practically impossible and arbitrary on this basis.*

TABLE 3

Variation in kinetic parameters (under different conditions)

Part A		4	5	5	2	2	2	3
Form of sample	4	9	10	20	9	9	9	3.1
Heating rate (K/min ⁻¹)	1152	3460	610-820	640-840	100	400	800	200
Sample mass (mg)	678-908	760-967	610-820	640-840	646-827	676-876	711-899	658-811
Temp. (°C)	9.73	17.12	17.23	16.41	20.21	15.41	14.12	19.95
ln A	154.80	230.24	203.72	208.39	230.25	201.37	194.53	234.98
E (kJ mole ⁻¹)	0.44	0.87	0.33	0.49	0.60	0.29	0.20	1.48
n	0.9986	0.9961	0.9923	0.9920	0.9792	0.9991	0.9996	0.9979
r eqn. (1)	-4.03	33.61	60.39	55.60	-67.68	26.24	9.87	31.06
ln A	20.52	394.75	592.23	568.73	-557.64	307.07	152.38	336.34
E (kJ mole ⁻¹)	0.38	1.04	0.38	0.58	-0.09	0.11	0.25	1.46
n	0.81	-0.78	-2.27	-2.16	3.33	-0.67	0.27	-0.71
m	0.9990	0.9979	0.9946	0.9957	0.9930	0.9996	0.9997	0.9982
r eqn. (2)	-0.95	33.76	26.95	50.49	-67.74	25.76	10.06	31.60
ln A	50.91	395.68	290.36	520.15	-557.48	302.18	154.40	341.19
E (kJ mole ⁻¹)	0.64	0.74	0.21	-8.41	1.35	-0.16	0.35	1.13
n	0.62	-0.77	-0.48	-1.82	3.31	-0.64	0.25	-0.74
p	0.9989	0.9983	0.9928	0.9957	0.9926	0.9996	0.9997	0.9982
r eqn. (3)	-7.08	24.36	67.74	53.82	-64.20	28.29	12.15	20.09
ln A	-10.16	298.85	659.84	551.58	-528.37	328.10	175.88	222.71
E (kJ mole ⁻¹)	-0.31	-0.95	0.60	0.24	-4.30	1.63	1.01	-32.73
n	2.71	4.72	-3.48	-1.09	13.00	-4.44	-1.83	76.68
m	-1.69	-4.92	0.77	-0.94	-9.73	3.61	1.92	-76.12
p	0.9991	0.9994	0.9951	0.9958	0.9933	0.9996	0.9998	0.9997
r eqn. (4)	ln A = a ₀ E + a ₁							
Part B	ln A = a ₀ E + a ₁							
a ₁	-6.0971	-5.7260	-5.2726	-6.2832	-5.4572	-5.1198	-5.4647	-3.3285
a ₀	0.1021	0.0999	0.1108	0.1090	0.1115	0.1020	0.1005	0.1022
r	1.0000	0.9998	1.0000	1.0000	1.0000	1.0000	0.9998	0.9962

Table 3 (continued)

<i>Part A</i>									
Form of sample	3	3	3	3	6	6	6	6	6
Heating rate (K min ⁻¹)	7.1	11.7	7.9	7.9	10	10	10	10	10
Sample mass (mg)	200	200	200	200	0.855	0.855	0.855	0.855	10.04
Temp. (°C)	699-867	690-880	762-902	762-902	625-775	625-775	625-775	625-775	638-875
ln <i>A</i>	25.77	13.33	13.54	13.54	13.21	13.21	13.21	13.21	13.38
<i>E</i> (kJ mole ⁻¹)	287.31	180.66	200.63	200.63	162.57	162.57	162.57	162.57	178.25
<i>n</i>	1.72	0.70	-2.52	-2.52	0.24	0.24	0.24	0.24	0.28
<i>r</i> eqn. (1)	0.9859	0.9893	0.9995	0.9995	0.9752	0.9752	0.9752	0.9752	0.9758
ln <i>A</i>	-54.91	-21.04	14.54	14.54	-17.83	-17.83	-17.83	-17.83	-18.48
<i>E</i> (kJ mole ⁻¹)	-467.22	-141.55	210.31	210.31	-102.92	-102.92	-102.92	-102.92	-113.25
<i>n</i>	0.96	-0.11	-0.01	-0.01	0.02	0.02	0.02	0.02	0.03
<i>m</i>	4.38	1.59	-0.05	-0.05	1.57	1.57	1.57	1.57	1.35
<i>r</i> eqn. (2)	0.9994	0.9995	0.9996	0.9996	0.9959	0.9959	0.9959	0.9959	0.9998
ln <i>A</i>	-56.44	-22.29	14.60	14.60	-21.36	-21.36	-21.36	-21.36	-30.29
<i>E</i> (kJ mole ⁻¹)	-480.56	-152.88	210.91	210.91	-131.26	-131.26	-131.26	-131.26	-218.14
<i>n</i>	2.91	0.57	-0.03	-0.03	0.56	0.56	0.56	0.56	0.41
<i>P</i>	4.43	1.63	-0.05	-0.05	1.65	1.65	1.65	1.65	1.74
<i>r</i> eqn. (3)	0.9993	0.9996	0.9996	0.9996	0.9943	0.9943	0.9943	0.9943	0.9995
ln <i>A</i>	-36.27	-32.77	18.57	18.57	-7.08	-7.08	-7.08	-7.08	-20.16
<i>E</i> (kJ mole ⁻¹)	-302.43	-247.20	243.82	243.82	-15.03	-15.03	-15.03	-15.03	-128.24
<i>n</i>	-18.34	7.07	-10.07	-10.07	-1.11	-1.11	-1.11	-1.11	0.08
<i>m</i>	47.69	-15.20	22.89	22.89	4.79	4.79	4.79	4.79	1.17
<i>P</i>	-43.95	17.18	-22.90	-22.90	-3.56	-3.56	-3.56	-3.56	0.24
<i>r</i> eqn. (4)	1.0000	1.0000	0.9999	0.9999	0.9972	0.9972	0.9972	0.9972	0.9998
<i>Part B</i>									
	ln $A = a_0 E + a_1$								
<i>a</i> ₁	-4.7460	-6.0021	-10.2021	-10.2021	-5.7217	-5.7217	-5.7217	-5.7217	-6.1565
<i>a</i> ₀	0.1068	0.1074	0.1179	0.1179	0.1174	0.1174	0.1174	0.1174	0.1099
<i>r</i>	0.9999	1.0000	0.9995	0.9995	0.9998	0.9998	0.9998	0.9998	1.0000

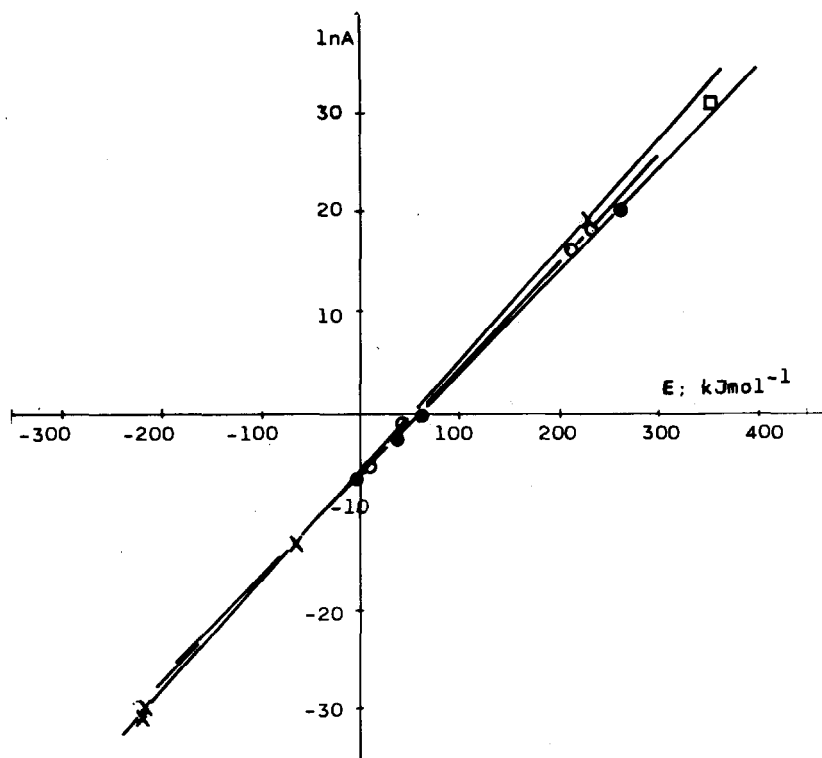


Fig. 2. The (C.E.)_i in the case of calcium carbonate. The kinetic constants were calculated by four different equations. ×, 200 mg; ○, 1000 mg; ●, 2000 mg; □, from industrial results.

The same conclusions can be deduced from Fong and Chen's [22] very accurate measurements and calculations, though they emphasized that "it is very difficult to determine the right reaction mechanism, because at least half of the tested $g(\alpha)$ functions give correlation coefficients higher than 0.995", and they chose $d\alpha/dt = k(1 - \alpha)^{1.5}$ as the kinetic expression describing the thermal decomposition of magnesium hydroxide. This choice is, however, really arbitrary because in the kinetic data they obtained using 17 various equations (Table 1), the correlation coefficient is higher than 0.981 in each case, and shows a C.E. (Fig. 3), which can be described with very high accuracy by the following relationship, for 15 sets of data points (with E in kJ mole^{-1}):

by Coats and Redfern's method

$$\ln A = 0.18919E - 6.6205 \quad (r = 0.9994)$$

by Satava's method

$$\ln A = 0.1799E - 6.1517 \quad (r = 0.9995)$$

These data indicate that the two methods give practically equivalent data.

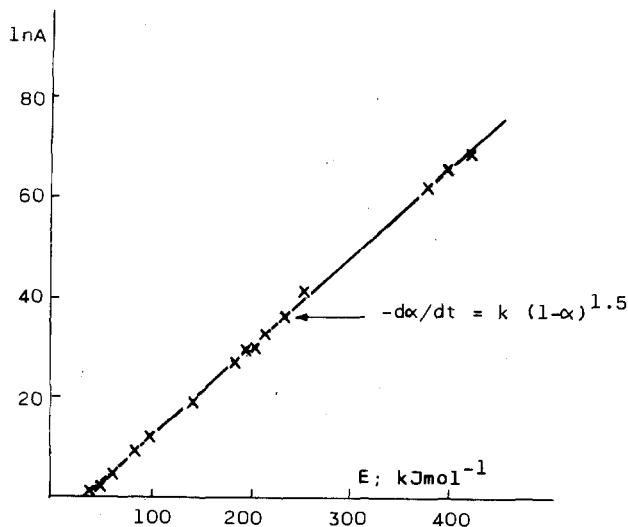


Fig. 3. The $(C.E.)_i$ in the case of magnesium hydroxide. The kinetic constants were calculated by 15 various differential equations.

On a similar basis it must be concluded that other methods must also be regarded as arbitrary choices (e.g., refs. 18, 20, 44). The thermal decomposition of calcium oxalate, kaolin, calcite, montmorillonite, and Marathon-coke was analysed by using 10 differential equations [21] and the C.E. was also demonstrated in all these cases. Figure 4 shows the calculated data for kaolin and calcium oxalate as examples.

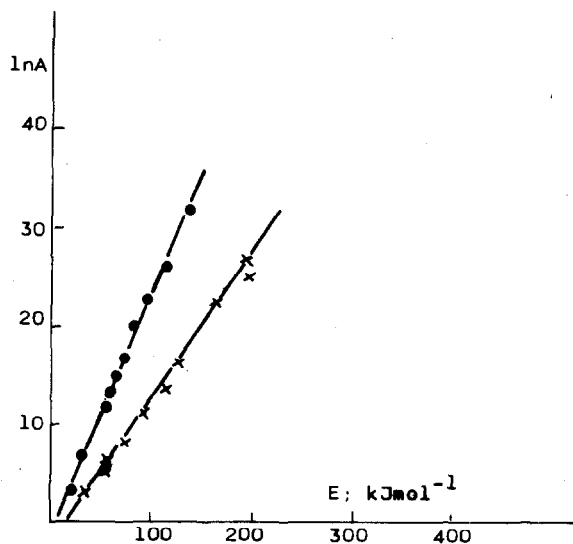


Fig. 4. The $(C.E.)_i$ in the case of kaolin and calcium oxalate. The kinetic constants were calculated by 10 different differential equations. ●, Calcium oxalate; ×, kaolin.

Connections between the logarithm of the pre-exponential factor and reaction order

It is necessary to extend the idea of the C.E. shown in the measurements reported here (Tables 2 and 3) because of the correlation between the activation energy (E) and the values of the different reaction orders (n, m, p).

The relationships between E vs. n , E vs. m , and E vs. p values are linear and, in contrast to the $\ln A$ vs. E function, they change more considerably with the measuring conditions. In addition to these relations, it follows from the C.E. that there is a relationship between the logarithm of the pre-exponential factor and reaction order.

There are also close relationships between the reaction orders and initially it would seem that these relationships are independent of the type of differential equation used for their calculation. The interdependence between n vs. m , n vs. p , and m vs. p values are shown in Figs. 5–7. The relation between the reaction orders was shown with reasonably high correlation coefficients. The value of r , for example, for n vs. m is higher than 0.8878 even in the case of linear regression and omitting the four extremely high values [see data in Table 3, eqn. (4) with sample form 3].

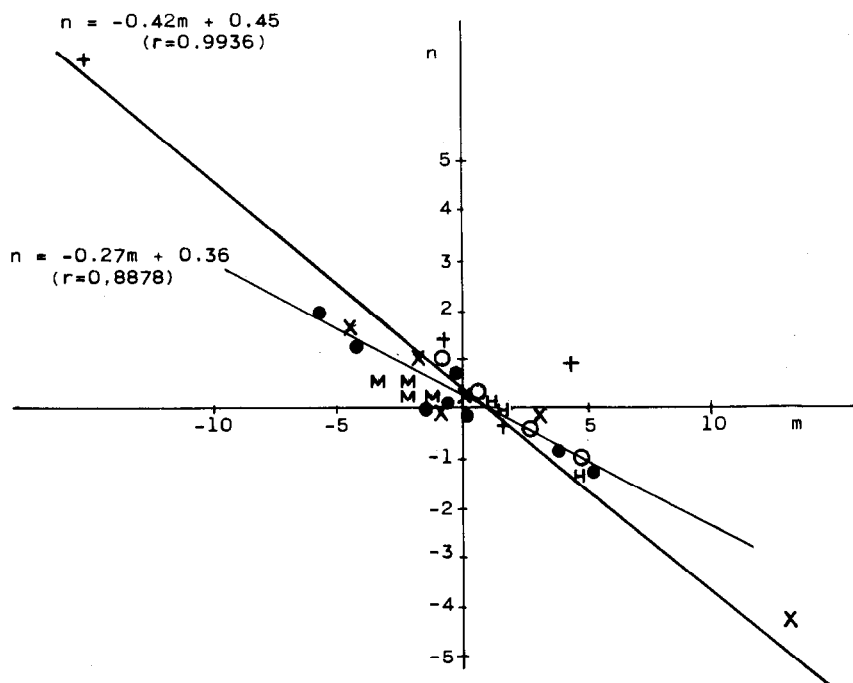


Fig. 5. The interdependence between the reaction orders n and m .

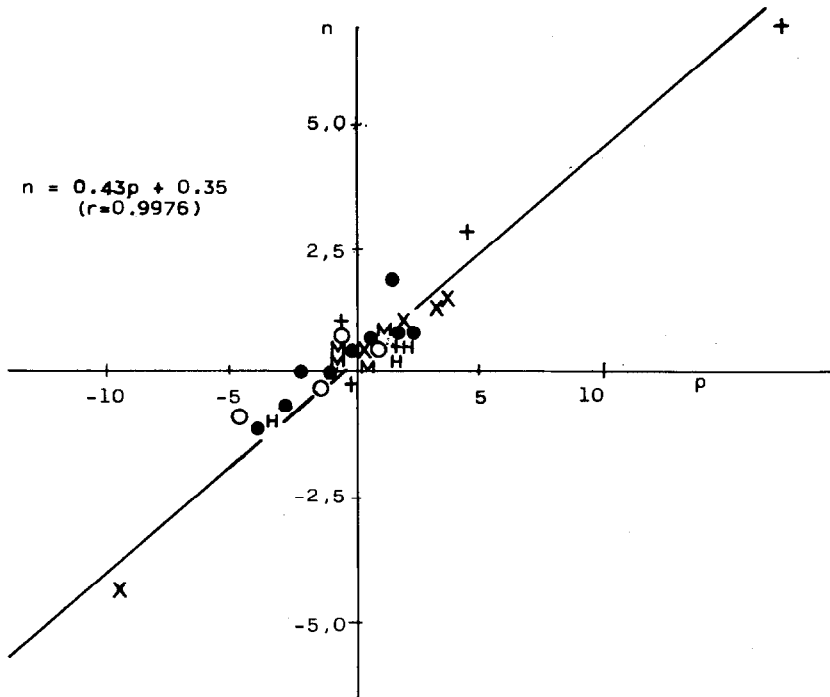


Fig. 6. The interdependence between the reaction orders n and p .

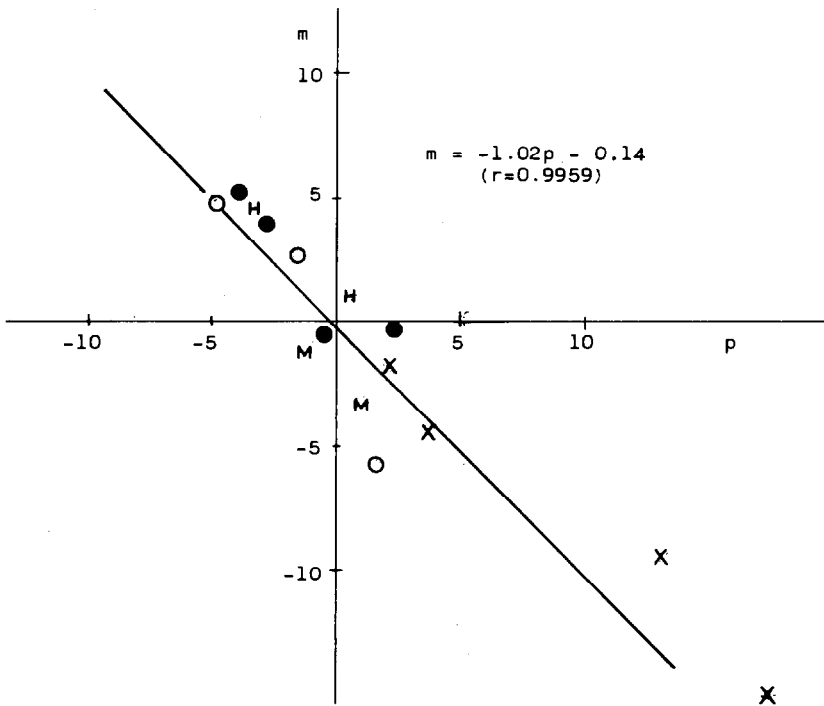


Fig. 7. The interdependence between the reaction orders m and p .

The constants of polynoms

The measured DTG curves as a function of time could be described by a sixth order polynom [eqn. (5)] with a high degree of accuracy.

$$\frac{-d\alpha}{dt} = A + Bt + Ct^2 + Dt^3 + Et^4 + Ft^5 + Gt^6 \quad (5)$$

A connection may be sought among these coefficients and this is shown in Figs. 8–11. These show a very close connection between the coefficients reminiscent of the C.E., though the values of these coefficients show significant modifications even if only one measured datum is eliminated without an appreciable decrease in the correlation coefficient.

DEDUCTIONS

The single coefficients of the polynom [eqn. (5)] have no direct physical meaning but they describe the DTG curves with great accuracy and show a close correlation with each other. This is an indirect verification of the very

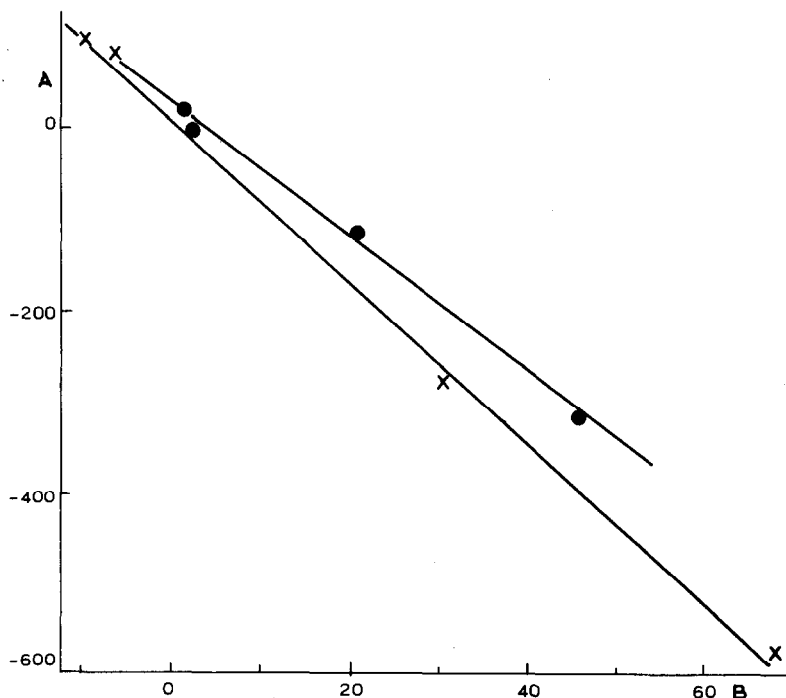


Fig. 8. The interdependence between the A and B coefficients of the polynom.

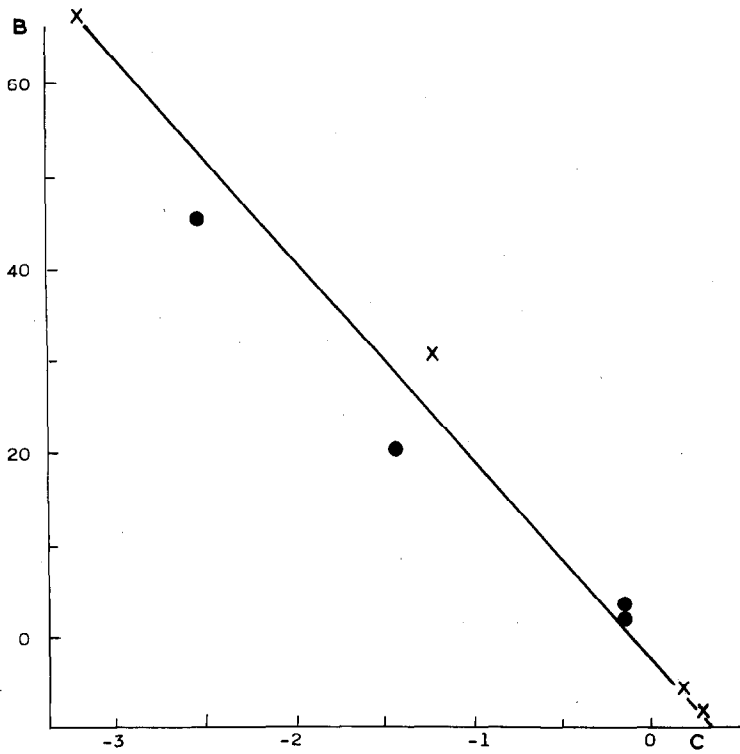


Fig. 9. The interdependence between the B and C coefficients of the polynomial.

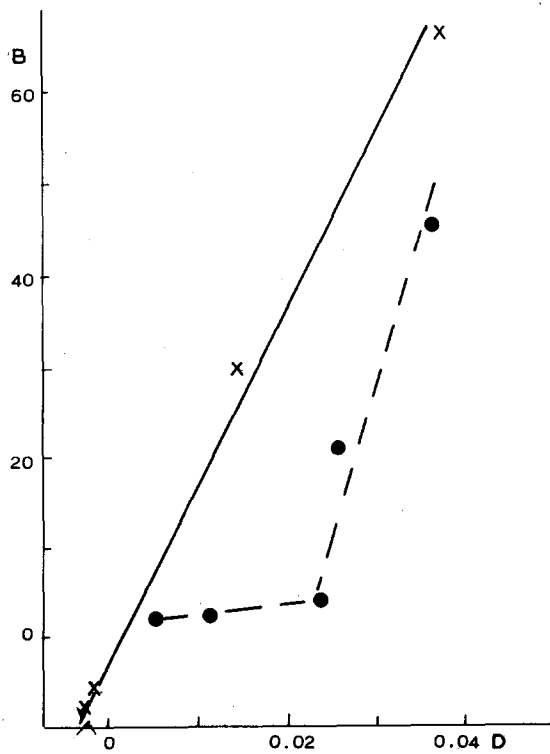


Fig. 10. The interdependence between the B and D coefficients of the polynomial.

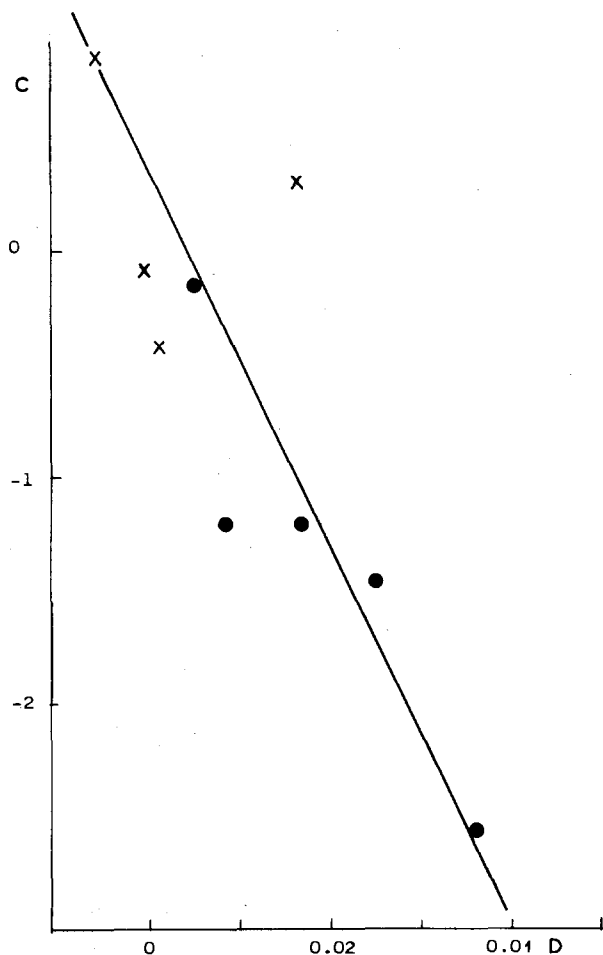


Fig. 11. The interdependence between the C and D coefficients of the polynomial.

formal descriptive character of the examined differential equations. It follows from the close correlation of the calculated kinetic constants that the activation energy can be used only together with the values of the suitable pre-exponential factor and the reaction order. In spite of this there are numerous publications giving only the activation energy values (e.g., refs. 18, 27, 45, 46). Criado and Morales [47] refer to this problem but from another aspect.

It follows from the strict correlation among the reaction orders (see Figs. 5–7) that there is no descriptive advantage of using more than three constants instead of A , E and n . The various suggested differential equations cannot reveal directly the mechanism of the examined thermal decomposition process. They are more complex and so they are not reducible to only one or a few rate determining processes in this way. On the basis of

theoretical and practical knowledge, eqn. (4) was expected to be the best one for the interpretation of the measured data for calcium carbonate decomposition, but of the equations tested in Tables 2 and 3 it seems to be the worst (e.g., the data for E). It is obvious that the idea incorporated in the equation is not wrong, but the practice of its development has not yet been found.

The experience obtained by the extreme change of the sample mass proves that the elimination of the superimposition of physical and chemical processes is impossible under the present measuring conditions. It is possible that, with presently available equipment, to raise such a requirement is not appropriate.

The close connection among the kinetic constants is a fact, consequently it is possible to change one of them with suitable modification of the others without the inevitable decrease in the fit of the description of the examined process. This can be proved to be so by examination of the literary data. Thus in spite of the views of Cremer [30], the main cause of the C.E. would not seem to be the unidirectional change of the entropy and enthalpy of activation, but due to the polynom-like very formal character of the differential equations. Consequently, *the calculation of the kinetic constants by the use of different differential equations or by changing one of the constants, for example the reaction order, in a suitable range can be used as a method to determine the (C.E.)_i, the ln A vs. E function of a single measurement. The (C.E.)_i as the compensation effect of the single measurement (in spite of the usual idea of the C.E.) seems to be very suitable for the examination of the measuring conditions on the investigated process giving some deeper qualitative and quantitative information about it.* The data shown in Tables 2 and 3, as well as in Fig. 2 show that the equation of the (C.E.)_i plot changes as a result. The slope of the plot can indicate the effect of the change of the sample mass and other parameters.

In relation to the problems cited by Garn above [27] it can be stated that the compensation effect should be anticipated in all cases, because it does not need any physical principles. Even if it can be a consequence of the lack of direct physical basis and its cause can be the structure of the descriptive system, its determination may still be instructive in deducing not only the nature of the temperature dependence but the effect of the measuring conditions generally.

SOME APPLICATIONS OF THE DEDUCTIONS

Indication of the change of the decomposition kinetics

According to the reports of Norris et al. [48], the k decomposition velocity is relatively insensitive to the exact value of the order of reaction n . The

TABLE 4
The effect of bromine compound on the degradation of the polyethylene terephthalate [49]

<i>n</i>	0%		5%		7%		9%	
	$\ln A$	E (kJ mole ⁻¹)	$\ln A$	E (kJ mole ⁻¹)	$\ln A$	E (kJ mole ⁻¹)	$\ln A$	E (kJ mole ⁻¹)
<i>Part A</i>								
0.5	34.90	192.13	15.04	91.94	10.96	69.21	28.75	170.44
1.0	57.71	311.37	38.58	220.94	24.17	140.80	49.31	281.98
1.5	80.53	430.40	62.12	349.89	37.32	212.35	69.83	393.56
2.0	103.36	549.94	85.65	478.89	48.78	283.95	90.25	505.10
<i>Part B</i>								
a_1	-1.8652		$\ln A = a_0 E + a_1$					
a_0	0.1914			-1.7366		-0.9266		-2.5411
r	1.0000			0.1825		0.1769		0.1838
				1.0000		0.9989		1.0000

alteration of the reaction order serves as a method to identify "the best kinetic constants", but it follows from the deductions made above that it is a method of determining the $(C.E.)_i$ plot, and this would serve to indicate the effect of the measuring conditions on the kinetics of the examined process. Table 4, for example, shows the effect of the retardant on the degradation of polyethylene terephthalate [49]. In this case the reaction order n was altered systematically between 0.1 and 2.0 looking for the best fit between the measured and calculated data. Part A of Table 4 shows some calculated kinetic constants [49] and part B the regression coefficients of the $(C.E.)_i$.

It is obvious from the regression coefficients (Table 4) that the data of the specimens containing a retardant form a group and the slopes of their $(C.E.)_i$ plots are characteristically different from the plot of the pure polyethylene terephthalate. From this it is concluded that the degradation kinetics have been modified by the retardant.

Other literary data also verify the usefulness of this method. Table 5 shows the computed regression coefficients of the $(C.E.)_i$ plots of some decomposition processes calculated by various orders of reaction between 0 and 2 [50].

As another example, the kinetic constants were calculated by different % conversion [38]. From the published data the regression coefficients of the $\ln A = a_0 E + a_1$ equation are

	Uncatalyzed	Catalyzed
a_1	-2.6410	-1.7256
a_0	0.2192	0.2295
r	0.9999	1.0000

TABLE 5

Regression coefficients of the $(C.E.)_i$ functions by changed reaction order [50]
 $\ln A = a_0 E + a_1$; $E(\text{kJ mole}^{-1})$

	$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$	NH_4BF_4	$(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ dehydration	$(\text{NH}_4)_2\text{C}_2\text{O}_4$ decomposition
a_1	-0.1289	-2.8784	-1.5643	-2.5605
a_0	0.2813	0.2126	0.3196	0.2359
r	1.0000	1.0000	0.9998	0.9999
$(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ dehydration			$(\text{NH}_4)_2\text{SO}_3$ decomposition	
a_1	-1.9243		-1.4070	
a_0	0.3465		0.3055	
r	1.0000		1.0000	

Consequently, the difference between the uncatalyzed and catalyzed (with *p*-toluene sulphonic acid) kinetics of the cyclization of a poly (*o*-hydroxy-amide) have been characterized by the parallel slip of the (C.E.)_i plots.

The C.E. and the homogeneous phase

In spite of a common current opinion in recent thermoanalytical literature that the C.E. in the heterogeneous phase is observable only as a result of experimental mistake or error in the evaluation, "relatively simple concepts have been very successful in explaining the C.E. of solvents and substituents on rates" of reactions in the homogeneous phase [51]. One cannot explain, however, the compensation between activation energy and pre-exponential factor in solution in terms of purely kinetic effects [51], and the problem is increased by the fact that the C.E. has also been observed in relationship with the concentration, moreover in the gas phase.

The decomposition of *m*-dichlorodiphenyl disulphide in solution serves as an example of the C.E. being observed in the liquid phase [52]. The decomposition temperature measured by the isoteniscope, and activation energy calculated by using the temperature dependence on the velocity of the increase in pressure, are shown in Table 6 as a function of concentration.

The activation energy changes with concentration but this change cannot be explained in terms of solvent-solute interaction; it is only understandable in terms of the C.E. (Fig. 12). The decomposition temperature depends unambiguously on the logarithm of the concentration.

As an example for the C.E. in the gas phase some collected data on the dimerization of cyclopentane are given in Table 7 [53-56]. A further example is the kinetic data on the thermal cracking of ethane and propane and their mixtures calculated by Froment et al. [57] which are plotted in Fig. 13. The measurements were made in a pilot plant looking for the effect of the total and the partial pressure under conditions representative of industrial operation. The authors found that the agreement with the industrial data were excellent but they made no comment on the C.E. It is obvious from Fig. 13, however, that the calculated data show the C.E. with a very good fit, indicating that the problems discussed above concerning the heterogeneous phase seem to exist in the homogeneous phase, too.

All this may be taken to express the complexity of the examined processes

TABLE 6

Decomposition of *m*-dichlorodiphenyl disulphide in solution [52]

% <i>m</i> -DDD	3	5	10	20	50	100
Dec. temp. (°C)	276.5	263.0	250.5	236.0	222.0	221.0
<i>E</i> (kJ mole ⁻¹)	347.52	212.70	150.73	149.48	162.46	158.68

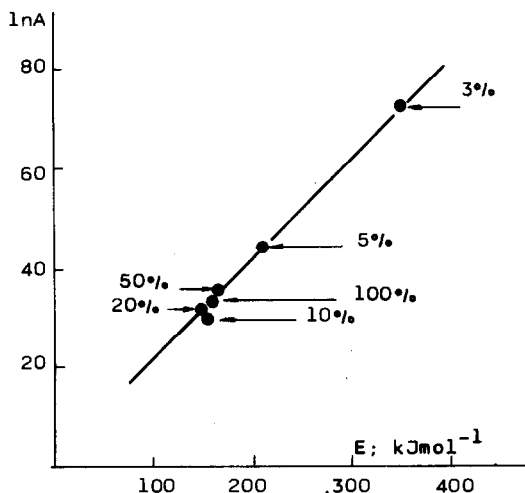


Fig. 12. The C.E. in the case of the decomposition of *m*-diphenyl disulphide in solution.

and that the mechanism of the chemical reaction is complicated both in the heterogeneous and homogeneous phase.

Thermogravimetric data and industrial processes

Because of its formal character eqn. (1) has been used for the description of some industrial experiences published in the literature [58], though the usual conditions of kinetic measurements cannot be assured under conditions of this industrial production. Using similar production systems and 200–300 μm particle size, the degree of decomposition of calcium carbonate was 10% in the pre-heater of one cement works at 790°C and about 60% at 845°C, whilst 80% decomposition was measured at 860°C in the pre-calcinator of another factory [58]. The Arrhenius parameters estimated from these data are: $\ln A = 31.6$ and $E = 351.27 \text{ kJ mole}^{-1}$, and these agree closely with the TG data showing a C.E. effect (Fig. 2).

Even the simplest extrapolation makes the relation likely between the thermogravimetric measurements and the industrial data. The temperature data for 10% and 90% conversion are shown in Fig. 14 as a function of the logarithm of the sample mass. Using these data, the extrapolated decomposi-

TABLE 7

Kinetic constants of the dimerization of cyclopentadiene

$\ln A$	14.16	14.48	14.98	15.53
$E \text{ (kJ mole}^{-1}\text{)}$	67.91	68.67	70.80	74.74

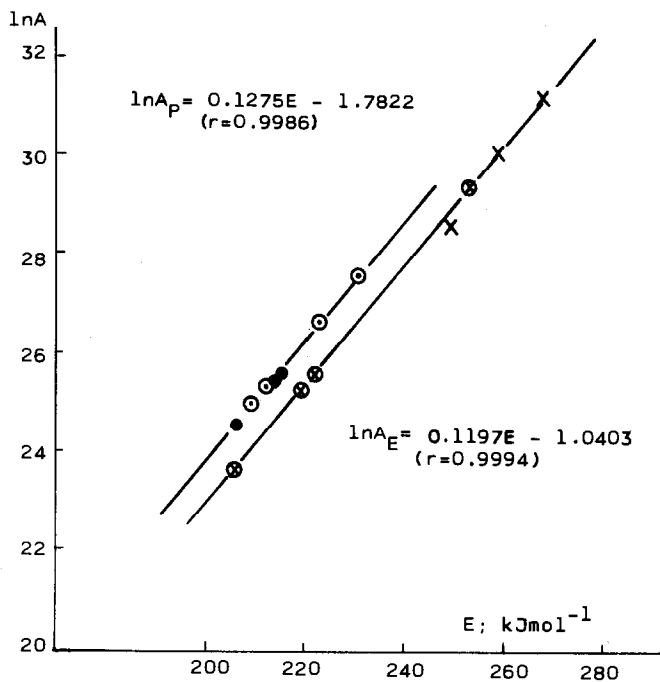


Fig. 13. Kinetic constants of the thermal cracking of ethane and propane and their mixtures. X, Ethane; ●, propane; ⊗, ⊙, mixtures.

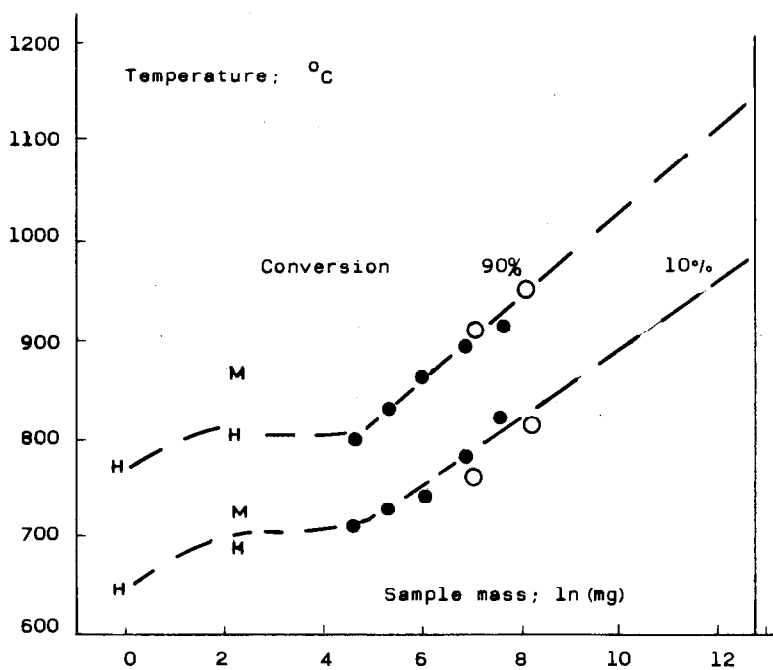


Fig. 14. Dependence of the decomposition temperature of calcium carbonate on the sample mass.

tion temperature of a 350 g sample seems to be 970°C and 1150°C, respectively, in good agreement with industrial practice.

A big difference exists between the conditions of the thermoanalytical measurements and the industrial processes, but it can be shown that they are related and this can be exploited in future work.

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