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SOME CONSIDERATIONS REGARDING THE KINETICS OF SOLID-STATE REACTIONS

J. Simon

Institute for General and Analytical Chemistry, Technical University, Budapest, Hungary

The present state of non-isothermal kinetics for solid-state reactions is discussed on the basis of the literature. Experimental data are given on the effects of sample size, heating rate, particle size and atmosphere on the thermogravimetric (TG) curve, as well as the values of the kinetic parameters calculated from them. One solution of the formal kinetics is introduced.

Thermal methods are often used to study the kinetics and mechanisms of solid-state reactions under isothermal and non-isothermal conditions. Although this subject is an important field of physical chemistry and its practical importance is well known, its problems have not yet been fully solved.

Reactions proceeding in homogeneous and in heterogeneous systems differ fundamentally from each other. Kinetic equations deduced for reactions taking place in homogeneous systems are theoretically never valid for those in heterogeneous ones. However, under given conditions such as constant reactant surface, etc., a similar treatment to that used in homogeneous systems can be applied for heterogeneous ones too. Of course, in thermal reactions occurring in the solid state, the contact surface changes continuously. This is the first and most important fact to be neglected when attempts are made to approximate to heterogeneous processes by kinetic characteristics calculated on the basis of thermal methods with the aid of the formalism established for the kinetics of homogeneous systems.

Thermal methods of analysis consist in measuring the changes in physical properties of the sample. Methods based on the measurement of weight or enthalpy are generally used. The former method is preferred due to its higher sensitivity and accuracy. Some time ago isothermal methods were preferred to dynamic ones. In recent years, however, the boundaries have become indistinct. On surveying recent publications one can observe the spreading of the combined application of isothermal and dynamic techniques, the comparison of results obtained by the two methods and the use of the dynamic technique alone.

The maintenance of constant temperature during measurements obviously ensures the constancy of the specific rate constant according to the Arrhenius equation [1]. This fact is also neglected when dynamic methods are used to study solid-state reactions. Apart from this, isothermal and dynamic methods encounter similar difficulties. One of these difficulties is the enthalpy change of the thermal decomposition of the substance studied, which is greatest during the reaction, and another the effect of gaseous decomposition products.

Dynamic methods are popular for several reasons, of which the following are worth mentioning:

a) They are rapid and their results easier to evaluate.

b) They can be used in a wide temperature range and allow the reaction to be followed over the entire range.

c) Informatory experiments, which are often necessary with the isothermal technique, can be omitted.

d) Several decomposition steps can be studied by means of one curve.

e) The theory and methods of evaluation have already been developed for the interpretation of curves obtained at linearly increasing heating rates.

The results obtained by the two methods have been compared in a number of papers and no significant differences have been found [2–6].

Omitting a detailed introduction, let us start with the differential equation valid for reactions proceeding under non-isothermal conditions:

$$g(\alpha) = \int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{AE}{Rq} \int_x^{\infty} \frac{e^{-x}}{x^2}\,\mathrm{d}x \tag{1}$$

where α = fraction reacted; g, f = symbols for function; A = pre-exponential term; R = gas constant; q = heating rate.

$$\int_x^{\infty} \frac{e^{-x}}{x^2} = p(x)\,. \tag{2}$$

The right-hand side of Eq. (1), called by MacCallum and Tanner [7] the "temperature integral", expresses the temperature-dependence of the specific rate constant.

Taking into account that the differential equation (2) cannot be integrated in finite form, a number of methods have been introduced to approximate the function.

The first approximation was that of Akahira [8]. The values of the integral $p(x)$ were later calculated by Doyle [9, 10] and Zsakó [11]. The different types of integration of function $p(x)$, involving critical comparisons too, were discussed by Šesták [12, 13]. Approximation formulae were given by Ozawa [14], MacCallum and Tanner [7], Šatava [15], Flynn and Wall [16] as follows:

$$\log p(x) = -2.315 - 0.4567x \tag{3a}$$

$$-\log p(x) = 0.4828\ E^{0.4351} + \frac{0.449 + 0.217}{T}\ 10^3 \tag{3b}$$

$$p(x) = \frac{e^{-x}}{x}\left[\frac{1}{x} - \frac{2!}{x^2} + \frac{3!}{x^3} - \frac{4!}{x^4}\right] \tag{3c}$$

$$p(x) = \frac{e^{x}}{x^2}\left[1 + \frac{2!}{x} + \frac{3!}{x^2} + \dots\right]. \tag{3d}$$

Most recently Biegen and Czanderna [17] dealt with the change of the value of the exponential integral. It was shown that the use of only the first term of the concomitant asymptotic series to approximate these integrals can result in less reliability than the uncertainty in the reaction data.

Accepting the table of log $p(x)$ values given by Zsakó as reference basis, and utilizing the various $p(x)$ substituting functions, in can be concluded that the approximation of MacCallum and Tanner [7] gives results which are closest to the data in the table, the deviation being in each case less than 1% [18].

The integral $p(x)$ can be resolved in finite form in the case where a hyperbolic temperature program is used [19–21], as follows:

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = -\frac{A}{b}\int_\infty^{1/T} e^{-E/RT}\,\mathrm{d}\left(\frac{1}{T}\right) = \frac{A\cdot R}{b\cdot E}e^{-E/RT} \tag{4}$$

where b is a constant which depends on the experimental conditions.

It can be stated on the basis of literature evidence that the accuracy of the integral methods (see Doyle [9], Coats and Redfern [26], Zsakó [11]) is higher than that of the difference-differential (Freeman and Carroll [27]) and approximation methods (van Krevelen [28], Horowitz and Metzger [29], Berlin and Robinson [30], Richer and Vallet [31]).

The relative standard deviation of the data obtained by the integral methods for the estimation of kinetic parameters of reactions taking place in the solid state is about 5–10%, depending on the value of x. The $g(\alpha)$ on the left-hand side of Eq. (1) is, by definition

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)}\,. \tag{5}$$

According to MacCallum's nomenclature [7], this expression is the "weight integral". $f(\alpha)$ is a certain function of the weight or of a term proportional to the weight. In practice the values of α are, in most cases, obtained from the thermogravimetric or differential thermoanalytical curves. The probable mechanism of individual cases of solid-state reactions can be expressed by the integral or differential forms of kinetic equations.

The form and number of equations used by different authors as kinetic functions or rate-controlling processes are quite different.

For the estimation of the probable mechanism of the reaction the apparent reaction orders $n = 0$ and 1 have only been used by Doyle [9]. According to Sharp and Wertworth [23] there is theoretical justification only for the reaction orders 0, 1/2, 2/3 and 1.

Zsakó [11] has used the relationship $f(\alpha) = (1-\alpha)^n$, with $n = 0$, 1/2, 2/3, 1 and 2.

Šatava and Škvara [32] give 9 equations for calculating the value of $g(\alpha)$, whereas Gallagher and Johnson [3, 4] use 18 equations.

A combined form of differential equation is suggested for the preliminary appraisal of the possible mechanism by Šesták and Berggren [33]:

$$\frac{d\alpha}{dt} = k \cdot \alpha^{m}(1-\alpha)^{n}[-\ln(1-\alpha)]^{p}. \tag{6}$$

It is interesting to note that whereas the mathematical methods of evaluation have greatly developed and the number of equations used to describe the rate-controlling process has increased, much less interest has been shown in the physical meaning of the evaluated kinetic parameters.

The kinetic equations are connected with the following processes: a. movement of phase boundaries; b. diffusion; c. nucleation; d. growth of nuclei.

Logically the above processes can be assumed to proceed. It would be interesting to make investigations with these processes.

The kinetic parameters (rate constant, pre-exponential term, activation energy, activation entropy) used for the description of heterogeneous reactions are explained analogously as for homogeneous ones. The rate constant is related to the impedance of the process, which must be overcome to achieve the new system. The pre-exponential term for homogeneous reactions contains the number of successful collisions of the molecule.

The activation energy is the amount of energy required for the substance to transform since, according to the Polányi–Wigner [34] theory, the starting molecules are separated from the products by a potential barrier corresponding to the activation energy. The activation entropy is the thermodynamic probability of the activated complex.

The relationships which show the direction of the changes in the kinetic parameters in the course of the rate-controlling process, or interpret the kinetic parameters on the basis of the knowledge of the given physical process and which lead to some conclusion, are not yet known. Further, the application of analogies in the interpretation of kinetic equations should be handled extremely carefully.

Draper and Sveum [36] do not agree with the statement that solid-state reactions are activated ones [35], saying that these reactions are not characterized by specific rate constants, are not temperature-dependent and, accordingly, have no activation energy.

In heterogeneous processes, in the case of endothermic decomposition the rate-controlling process can be characterized by the following expression:

$$1-(1-\Phi)^{2/3} + 2/3\left(\frac{\kappa - hr_0}{hr_0}\right) = \frac{4\pi r_0 M\kappa\beta}{3 g_0 \Delta H_{TR}} t^2 \tag{7}$$

where Φ = fraction reacted; h = heat transfer coefficient; κ = thermal conductivity of the product; r_0 = initial radius of the spherical sample; T_R = temperature of reaction; β = linear heating rate; M = molecular weight of the reactant; g_0 = initial weight of the sample; t = time, Furthermore, it is assumed that the solid-state reaction proceeds at constant temperature T_R and the rate-controlling processes are dependent on the heat transfer. The authors have found good agreement for some endothermic decompositions. It is important to note that the equation is valid for samples with spherical geometry. This idea of the use of spherical samples can be found in the papers of several authors [23, 37–39].

The first term on the left-hand side of Eq. (6). agrees with that characterizing a process taking place according to the contracting geometry law.

It is also noteworthy that this relationship was found to fit best for a number of reactions [4, 24, 41–44]. On the basis of what has been said it can be concluded that there is some inconsistency in the theoretical interpretation of solid-state reactions [45].

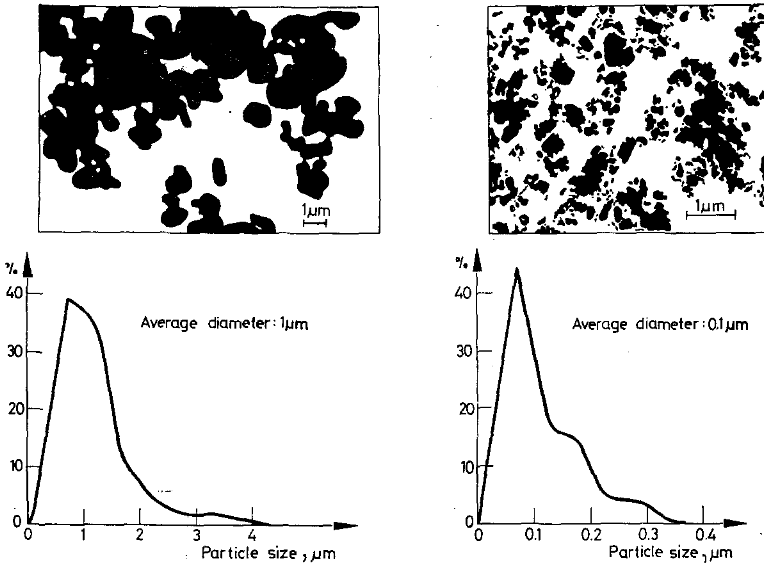

Fig. 1. Electron micrographs and particle size distribution curves of $Ca(COO)_2 \cdot H_2O$ [25]

The basic problem is whether there exist experimental conditions which ensure the complete predominance of various rate-controlling processes, or only the problems of heat transfer in solid substances are encountered when the experimental conditions favour the formation of an apparent rate-controlling process.

As shown by literature data and our experience, the experimental conditions strongly affect the shapes of the thermal curves and consequently the kinetic parameters calculated on the basis of these curves. The effects of sample size [3, 5, 23, 24, 40, 48, 49, 51], heating rate [3, 5, 25, 46, 47, 51, 52], particle size [24, 41, 44] and atmosphere [44, 50, 51] have been investigated.

The dehydration of calcium oxalate monohydrate [$Ca(COO)_2 \cdot H_2O$] has been investigated by several authors [53–56]. To demonstrate the effect of the experimental conditions let us study the series of TG curves taken with the Derivatograph [57] representing the dehydration of this compound. The effect of sample size was studied on 70, 200, 300 and 1000 mg samples, at heating rates of 1, 5 and 10°/min.

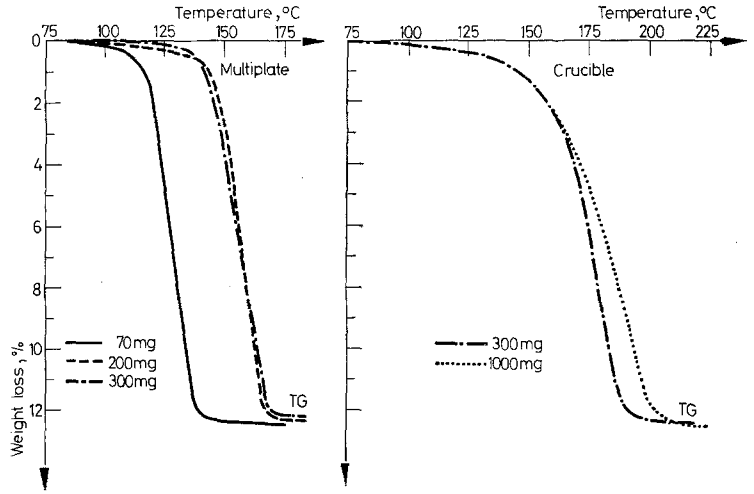

Fig. 2. Crystallized $Ca(COO)_2 \cdot H_2O$. Effect of sample size. Heating rate 1°/min

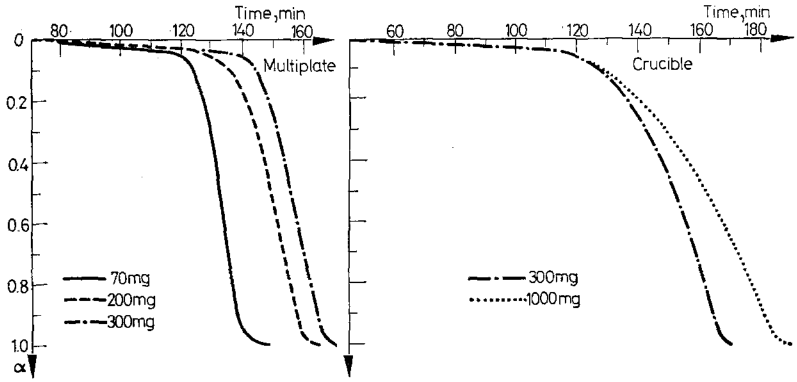

Fig. 3. Crystallized $Ca(COO)_2 \cdot H_2O$. Effect of sample size. Heating rate 1°/min

In order to investigate the effect of layer thickness on the decomposition, the samples were either sieved onto a multiplate sample holder consisting of 10 Pt plates [58] or weighed into a Pt crucible.

The effect of the atmosphere was studied using a special labyrinth-crucible [59] in which the self-generated atmosphere could be ensured.

The influence of particle size was studied using $Ca(COO)_2 \cdot H_2O$ samples with different particle sizes (Fig. 1).

Table 1

Ground $Ca(COO)_2 \cdot H_2O$. Values of E and n for different sections of the TG curve as a function of the experimental conditions

Heating rate (°C/min)	1	5	10	1	5	10	1	5	10	1	5	10
Sample size (mg)	70	70	70	200	200	200	300	300	300	300	300	300
Sample holder	Pt plate	Pt plate	Pt plate	Pt plate	Pt plate	Pt plate	Pt plate	Pt plate	Pt plate	Pt crucible	Pt crucible	Pt crucible
Apparent activation energy E, kcal/mole, and reaction order (n)												
Full curve	40	37	36	37	29	28	31	22	18	29	22	21
$\alpha = 0.01-0.95$	(2)	(2)	(2)	(1)	(1)	(1)	(1)	(2/3)	(2/3)	(1)	(1)	(1)
Linear section	53	36	30	45	35	30	40	31	26	27	23	22
$\alpha = 0.15-0.9$	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)
Lower part	15	14	14	14	14	14	14	16	16	15	14	14
$\alpha = 0.7-1$	(0)	(1)	(1)	(2/3)	(2/3)	(2/3)	(1/2)	(2/3)	(1)	(2/3)	(1)	(2/3)

Fig. 2 shows the effect of sample size. The smaller the sample size, the narrower is the temperature interval $(T_f - T_i)$ of the decomposition. $(T_f - T_i)$ increases, and the slope of the curve decreases with increasing sample size.

If this effect is studied on the basis of the α vs. time function, we find that the smaller the sample size the smaller is the reaction time (Fig. 3).

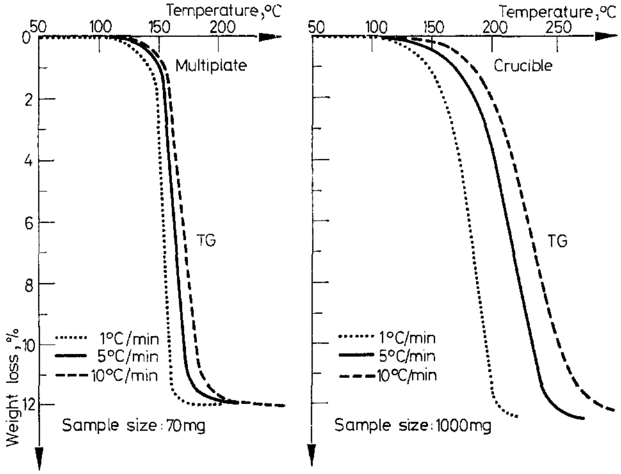

Fig. 4. Crystallized $Ca(COO)_2 \cdot H_2O$. Effect of heating rate

The effect of heating rate is demonstrated in the extreme sample sizes used in our present work (Fig. 4). The $(T_f - T_i)$ interval is also dependent on the heating rate. The slope of the curve decreases with increasing heating rate. If this effect is plotted in an α–t diagram (Fig. 5), it can be concluded that the reaction time decreases with increasing heating rate.

Table 2

Crystallized $Ca(COO)_2 \cdot H_2O$. Values of E and n

Heating rate (°C/min) Sample size (mg) Sample holder	1 70 Pt plate	5 70 Pt plate	10 70 Pt plate	1 200 Pt plate	5 200 Pt plate	10 200 Pt plate
	Apparent activation energy E, kcal/mole					
Linear section $\alpha = 0.1-0.9$	66 (2/3)	51 (1)	35 (2)	45 (2/3)	40 (1)	31 (1)

The effect of particle size is shown in Fig. 6. It can be observed that in the case of smaller particle size the reaction proceeds in a narrower temperature interval, within a shorter period of time.

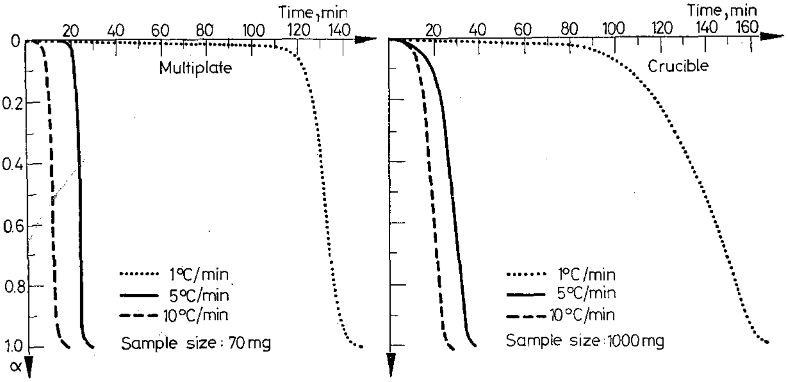

Fig. 5. Crystallized $Ca(COO)_2 \cdot H_2O$. Effect of heating rate

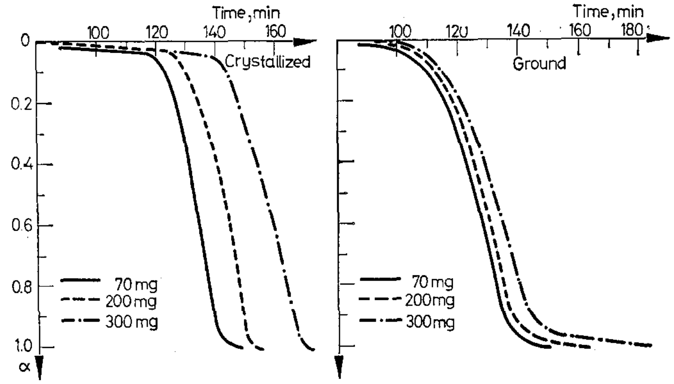

Fig. 6. $Ca(COO)_2 \cdot H_2O$. Effect of particle size. Heating rate 1°/min

as a function of the experimental conditions

1	5	10	1	5	10	1	5	10
300	300	300	300	300	300	1000	1000	1000
Pt	Pt	Pt	Pt	Pt	Pt	Pt	Pt	Pt
plate	plate	plate	crucible	crucible	crucible	crucible	crucible	crucible

and reaction order (*n*)

38	29	30	24	24	18	23	16	16
(1/2)	(2/3)	(1)	(1/2)	(2/3)	(2/3)	(1)	(2/3)	(1)

The effect of the atmosphere is shown in Fig. 7. The time of reaction becomes shorter as the rate of heating increases. The reaction takes a longer time in the labyrinth-crucible, especially in the case of a heating rate of 1°/min.

In Figs 8 and 9 idealized TG curves demonstrate the effects of changes in the slope of the curve on the activation energy and order of reaction.

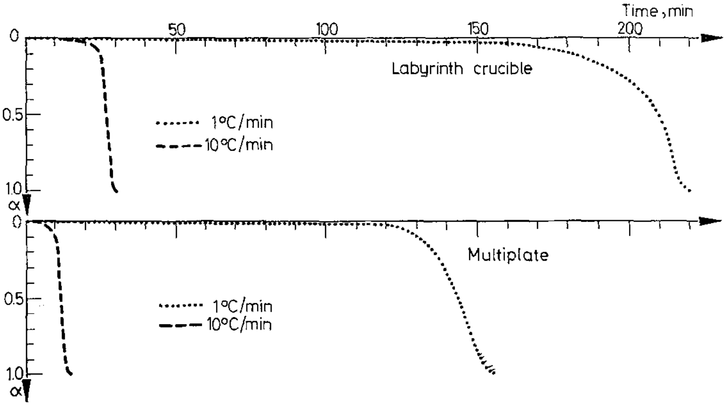

Fig. 7. Crystallized $Ca(COO)_2 \cdot H_2O$. Comparative diagram for the effect of atmosphere Sample size: 200 mg

What has been said, as well as literature data demonstrate the great influence of the experimental conditions on the shape of thermogravimetric curves. The trend of the changes, however, is always similar. Accordingly, the changes in the values of the parameters calculated from the curves also show a definite trend.

In Table 1 the values of the activation energy and reaction order are given for the different sections of the TG curve as calculated from the kinetic parameters obtained under the given experimental conditions. It is interesting to observe that a uniform reaction order is obtained only for the nearly linear portion of the curve.

In the case of crystalline Ca-oxalate monohydrate no uniform reaction order can be obtained even for the linear section, although the trend of the activation energy is similar to that in the former case (Table 2).

In Table 3 the values of the activation energy and order of reaction are given as calculated by different methods. The data in the Table reflect that the activation energy decreases with increasing sample size and heating rate; this can be accounted for by the kinetic compensation laws [60] and by the change of the distribution of thermal flux.

Gallagher and Johnson [4] have investigated whether the activation energy can be extrapolated to zero sample weight and have stated that the logarithmic dependence upon weight precludes extrapolation to zero weight.

Dharwadkar and Phadnis [47] suggest the application of a temperature transformation to eliminate the dependence of the kinetic parameters on the experi-

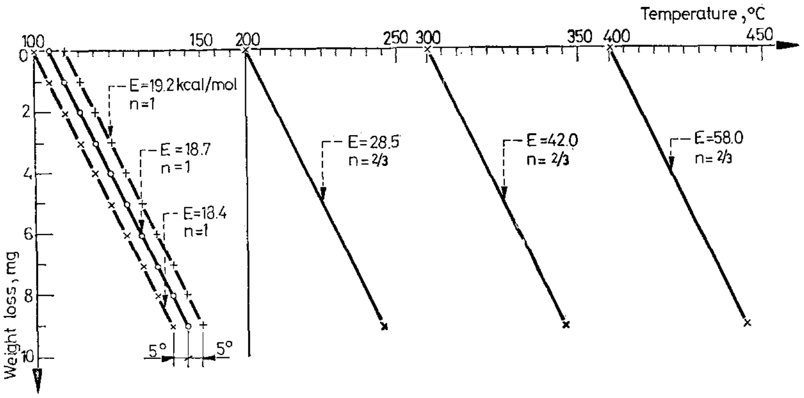

Fig. 8. Theoretical curves. Change of the numerical values of E and n supposing parallel lines

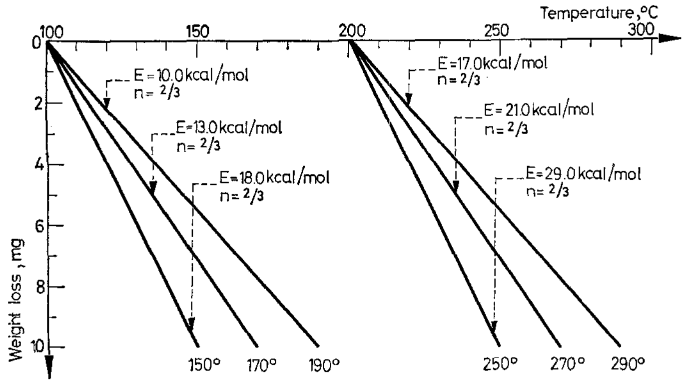

Fig. 9. Theoretical curves. Change of the numerical values of E and n supposing non-parallel lines

mental environment. In a weight vs. temperature graph the effect of the experimental conditions is exhibited by a change in the temperature interval $(T_f - T_i)$ of the TG curve. The authors define a temperature T':

$$T' = T + \Phi, \quad \text{where} \quad \Phi = \frac{T - T_i}{T_f - T_i} \cdot 100 .$$

On inserting the temperature defined in this way into the Coats–Redfern [26] equation, the changes in the value of the activation energy become smaller. The values obtained for the activation energy by the method described are presented in Table 3.

In the case where the slopes of the curves are markedly different, however, the shift along the abscissa does not result in even a formal resolution of the problem. Summing up what has been said, it can be stated that no satisfactory solution can be found within the framework of formal kinetics.

It seems probable that one resolution of formal kinetics might be the use of

Table 3

Ground $Ca(COO)_2 \cdot H_2O$. Values of E and n obtained by different methods of evaluation

Heating rate (°C/min) Sample size (mg) Sample holder	1 70 Pt plate	5 70 Pt plate	10 70 Pt plate	1 200 Pt plate	5 200 Pt plate	10 200 Pt plate	1 300 Pt plate	5 300 Pt plate	10 300 Pt plate	1 300 Pt crucible	5 300 Pt crucible	10 300 Pt crucible
Difference—differential method (Freeman—Carroll)	67 (2.3)	47 (1.9)	33 (1.5)	60 (1.7)	41 (1.5)	32 (2.5)	46 (2.3)	38 (2.4)	29 (2.1)	33 (2.1)	29 (2.0)	20 (2.3)
Integral method (Zsakó)	53 (1)	36 (1)	30 (1)	45 (1)	35 (1)	30 (1)	40 (1)	31 (1)	26 (1)	27 (1)	23 (1)	22 (1)
Approximate methods	30—60						20—40					
Improved method Coats—Redfern—Dharwadkar	20.7	21.7	22.9	25.3	23.9	24.6	24.3	20.5	22.4	25.2	21.0	23.7

experimental conditions, the effect of which can be neglected to a first approximation; in other words the error due to this does not exceed that of the mathematical methods of evaluation. From this point of view it seems reasonable to study very small samples (≤ 1 mg) of very small particle size (≤ 0.1 μm) at a small heating rate ($\leq 0.5°$/min), possibly in a self-generated atmosphere. According to the literature [4] even TG curves thus obtained do not coincide, but the curves–especially the linear sections–are nearly parallel, that is, the slope of the curve only changes slightly. In these circumstances the temperature transformation becomes justified.

An approximation of this type might mean the standardization of the experimental conditions, in other words, the results of measurements made in different laboratories could be compared. This would mean the solution of the problems of formal kinetics. Furthermore, the effect of the experimental conditions should be eliminated when the existence of the different rate-controlling processes is studied.

The study of the formal kinetics law is the first step, but for a more extensive interpretation it is necessary to know about the relations of real kinetics, which is a task for the future.

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RÉSUMÉ — On discute, à partir des données de la littérature, l'état actuel de la cinétique non-isotherme des réactions en phase solide. On donne ensuite quelques résultats d'expérience montrant l'influence de la prise d'essai, de la vitesse de chauffage, de la granulométrie et de l'atmosphère sur la courbe thermogravimétrique et sur les paramètres cinétiques calculés. On introduit une solution de cinétique formelle.

ZUSAMMENFASSUNG — Der gegenwärtige Stand der nicht isothermen Kinetik von Reaktionen in festem Zustand wird an Hand der Literatur erörtert. Außerdem werden einige Versuchsergebnisse bezüglich der Wirkung der Einwaage, der Aufheizgeschwindigkeit, der Teilchengröße und der Atmosphäre auf die thermogravimetrische (TG) Kurve, sowie der Wert der aus ihr errechneten kinetischen Parameter angeführt. Eine formalkinetische Lösung wird eingeführt

Резюме — На основании литературных данных обсуждено современное состояние неизотермической кинетики для твердофазных реакций. Приведены также некоторые экспериментальные данные о влиянии размера образцов, скорости нагрева, размера частиц и атмосферы на термогравиметрические кривые (ТГ) и величины кинетических параметров, расчитанных по ним. Представлено решение формальной кинетики.