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THE PROBLEMS OF REACTION KINETICS CALCULATIONS BASED ON THERMOANALYTICAL CURVES

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ABSTRACT

The work, results and estimations are summarized which are related to reaction kinetic calculations using thermoanalytical curves. Mathematical operations applied to the calculations are studied. Calculation methods are evaluated on the basis of our test results. The effect of test conditions on reaction kinetic parameters is analysed. Calculation of half-period is also investigated in the study.

INTRODUCTION

Most thermoanalysts maintain that the Arrhenius equation, which applies to thermal reactions under isothermal conditions, can also be applied to heterogeneous reactions carried out under non-isothermal conditions. Nevertheless, there is another opinion that the Arrhenius model is not suitable for the kinetic or formal kinetic evaluation of thermogravimetric curves [1]. The present work discusses, on the basis of our published results, these contradicting views.

The major factor which led to doubts concerning the validity of the Arrhenius model is that the thermogravimetric curves recorded under different experimental conditions are extremely dissimilar, because under certain conditions the transformation process (or, its kinetics) depends primarily, not on the chemical reaction proper, but rather on much slower elementary physical processes (e.g. low heat conductivity, slow diffusion of the evolved gaseous products, nucleation, nucleus growth, recrystallization, etc.). A previous publication [1] showed several TG curves of the same calcium carbonate sample. The curves, recorded under different conditions, were indeed very dissimilar. The authors indicated that, in agreement with the findings of others, the parameters of the reaction kinetics equation constructed for this dynamic system could not be evaluated with sufficient certainty. Their claim, however, was not substantiated by experimental data, either their own or those taken from the literature. In our opinion their claim is based on

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theoretical derivation, the cornerstone of which is the dissimilarity of TG curves recorded under different conditions.

CALCULATIONS OF REACTION KINETICS CARRIED OUT ON DERIVATOGRAPHIC CURVES OBTAINED WITH CONTINUOUS HEATING

The problems of calculations of reaction kinetics have been extensively studied in our Institute. This presentation summarizes some of the major results.

The mathematical operations used in the calculations

In the early work, the mathematical calculations were studied, with the aid of which different authors—taking the rate equation and the Arrhenius equation (which describes the temperature dependence of the rate constant) as starting points—attained relations which are suitable for the evaluation of the activation energy, and the reaction order from the data of thermoanalytical curves [2–6]. In the course of demonstrations, most authors made an effort to eliminate the terms which can be determined only with difficulty from the thermoanalytical curves. According to the mathematical derivation used, the methods applied and investigated by us for the determination of the activation energy, can be divided into three main groups [6].

The first group involves methods which do not solve the basic differential equation

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = Z\,\mathrm{e}^{E^{x}/RT}C^{n} \qquad (1)$$

Rewrite it in logarithmic form [7], then take the difference of the logarithmic equations written at different points in time [8].

Methods which belong to the second group attempt the solution of the basic differential equation, i.e. by using different assumptions they integrate the basic equation, then take the logarithm of the expression just obtained. The methods published by Horowitz and Metzger, methods I and II, [9] and Zsakó [10] belong to this group.

The methods which belong to the third group, including the method of Kissinger [11], take the time derivative of the basic differential equation, introduce several substitutions and, after several mathematical steps, apply successive integration, logarithmation and differentiation steps to obtain the final formula. Each of the equations obtained is a function. Straight lines are obtained when the corresponding x–y points of these functions are plotted. The activation energy can be calculated from the slope of the line. In certain cases it is possible to calculate the reaction order [8] and the frequency factor [7] from the point of intersection of the line with the y-axis.

There are also several possibilities for the determination of the reaction order (n). The method of Freeman and Carroll [8] has already been mentioned. According to Horowitz and Metzger [5,9] the reaction order can be derived, with a suitable calibration curve, from the concentration belonging to the inflexion point of the TG curve.

Kissinger [5,11] maintains that the reaction order can be calculated from the $n = 1.26\sqrt{s}$ relationship. Here s is related to the so-called shape index, the calculation of which is detailed by the author. Hüttinger [5,12] starts with the basic equation, but his sole purpose is the determination of the reaction order. He introduced the rate of heating into the equation as an additional parameter, and developed two methods for the determination of the reaction order. The first is the so-called differential method. Here, the basic equation is successively applied for the rate of gas evolution, at two different heating rates. The first equation is divided by the second, and the logarithm of the result is taken. When the corresponding x–y values of this function are plotted, then the reaction order can be determined from the slope of the straight line. The other process is an integral process. The basic equation is generated at two different heating rates, then the first expression is divided by the second, and both sides of the resulting equation are integrated.

Critique of the calculation methods

Following the review of the methods of calculation, their critical evaluation has been attempted with the aim of selecting the simplest, yet most suitable relationship. Also, an expression has been sought in which the effects of experimental errors are minimized.

The expression proposed by Selmeczi [7] proved difficult in actual practice, because the calculation of activation energy required the reading of the corresponding T_i temperature–s_i weight loss, T_i temperature–h_i DTG galvanometer deflection values off the derivatogram, and the separate knowledge of the calibration factor of the DTG galvanometer and also the reaction order. Though both the calibration factor [13] and the reaction order can be determined experimentally, their determination requires further time. An advantage of the method is that once the necessary data are known, then the frequency factor, Z, can also be calculated.

Compared with all the other methods the drawback of Zsakó's process [10] is that the reciprocal temperature has to change linearly in time. Therefore, the program settings used for the kinetic measurements differ from those of the regular operation [14]. Derivatograms recorded by the usual linear heating programs cannot be used for the calculations.

Kissinger's method [11] developed for the calculation of the activation energy is apparently a simple one. While all the other methods require the knowledge of the concentration change as a function of temperature, here only the peak temperatures which correspond to the various heating rates need to be known. However, the drawback of the method is that the peak temperature has to be known more accurately then is usually measured in derivatography. This conclusion is also substantiated by our results, which were obtained during a decomposition study of trichlorphon [15–17]. Another drawback is that several derivatograms are required for the evaluation.

The equation proposed by Horowitz and Metzger (method I) [9,17] is suitable only for first-order reactions, or for decompositions where the decomposition products are gaseous and immediately leave the studied system. If the reaction is not of first order, or liquid or solid intermediates are formed during the decomposition, then the second equation of Horowitz and Metzger (method II) should be used for the determination of the activation energy. Thus, before attempting the evaluation, the reaction order, or the decomposition mechanism has to be determined.

While studying the decomposition kinetics of trichlorphon [15–17] it was concluded that errors in the determination of peak temperatures or the reaction order do not cause significant errors in the activation energy when the Horowitz–Metzger method is used. However, the error becomes quite large when overlapping processes are studied and the "concentrations" belonging to the individual T_i temperatures cannot be determined accurately.

Freeman and Carroll [8] developed a method for those reactions in which solid and volatile decomposition products are formed. They make use of the difference of the logarithmic values, consequently the absolute values of the parameters (concentration, weight-loss rate) do not have to be known, only those parameters which are proportional to them, such as the weight loss (w_i) or the deflection of the DTG galvanometer (h_i). Therefore, the method can also be successfully used for overlapping processes [15–17]. In this case, the error of the h_i and w_i readings is eliminated when the weight loss and its rate arising from the latter decomposition process is proportionally superimposed onto the weight loss (w_i) and decomposition rate of the previous process. This method is especially advantageous, because it makes direct use of the DTG curve (there is no need for calibration factors). To the best of our knowledge, we were the first to report this observation (Freeman and Carroll used the TG curves). The method does not even necessitate a knowledge of the reaction order, in fact the reaction order can be determined by this method. Since the Freeman–Carroll method gave the most reliable activation energy values, even for overlapping decomposition processes, these values are used in the discussion of the results.

Due to their simplicity, all three methods, i.e. Freeman–Carroll's, Horowitz–Metzger's and Kissinger's, were used for the determination of the reaction order [16,17]. In our experience, the latter two gave identical results, while those obtained using the method of Freeman and Carroll differed sometimes. Therefore, if there are doubts concerning the reaction orders determined by the Freeman–Carroll method, it is advisable to check them by the other two simple methods.

Reflection of change of experimental conditions in the reaction kinetic parameters

Having decided which methods gave the most reliable results in the simplest possible way, the effects of the experimental conditions upon the reaction-kinetical parameters, especially that of the heating rate, were examined. The different decomposition types of three compounds: nickel(II)-hexammin-chloride, polystyrene-divinylbenzene copolymer and trichlorphon (O,O-dimethyl-1-hydroxy-2,2,2-trichloroethylphosphonate) were used for the study [17]. A 9 mm upper diameter platinum crucible, equipped with a lid, was used during the derivatographic measurements, which were carried out in flowing nitrogen atmosphere. Two-hundred-mg samples were used, except for trichlorphon, of which only 100-mg samples were used. It can be seen from our previous results [17] (cf. Table 1, Freeman–Carroll's method) that the activation energy changes for a while with increase in heating rate. (In the case of nickel(II)-hexammin chloride and trichlorphon, when the type of the reaction is solid $\xrightarrow{\text{heat}}$ solid + gas, melt $\xrightarrow{\text{heat}}$ liquid + gas, respectively, the activation energy decreases. In the case of the polystyrene-divinylbenzene copolymer, when the reaction type is a solid $\xrightarrow{\text{heat}}$ gas + gas, it increases). Above certain heating rates the activation energy levels off, and remains constant. Using small sample sizes (200 mg), constant activation energy values were obtained at and above 5°C min^{-1} heating rates. With the trichlorphon melt, where the sample was only 100 mg, 2°C min^{-1} heating rates were sufficient to produce constant values.

It is fortunate that two of the three compounds have also been studied by others, thus making a comparison of the activation energies possible. Murgulescu and Segâl [18] studied the decomposition kinetics of nickel(II)-hexammin-chloride under isothermal conditions. According to them, the activation energy of the first decomposition step is 60.03 kJ mole^{-1}, which is in excellent agreement with our 60.29 kJ mole^{-1} (5.1°C min^{-1}) and 59.45 kJ mole^{-1} (9.2°C min^{-1}) values. Rübakov and Ermiskin [19] used polarographic and potentiometric methods for the determination of the decomposition activation energy of trichlorphon in solutions. Their value is 103.83 kJ mole^{-1}, which again agrees well with our 98.39 kJ mole^{-1} (2.2°C min^{-1}), 96.28 kJ mole^{-1} (7.4°C min^{-1}) and 97.13 kJ mole^{-1} (11.1°C min^{-1}) values. (The data shown in parantheses refer to the heating rate.)

I would like to mention at this point our results which were obtained for the decomposition of calcium carbonate derived from organic calcium salts, and in general our results which were gained for the decomposition of calcium carbonate. The amount of calcium carbonate formed of the same mass of the organic calcium salt depends on the molecular weight of the given salt. The parameters of the kinetics of the decomposition of calcium carbonate obtained by heating 200-mg salt samples were determined from the thermal curves recorded at a heating rate of 5°C min^{-1}. The amount of

TABLE 1

Thermal characteristics of calcium carbonate samples of different origin

Salt	Mass of $CaCO_3$ (mg)	Heating rate (°C min^{-1})	DTG peak temp. (°C)	Activation energy (kJ $mole^{-1}$)	Reaction order	$\tau_{1/2}$(700°C) (min)
Calcium carbonate, p.a.	50	10	805	177.52	0.54	28.02(14.15)
Calcium carbonate, p.a.	200	5	905	159.93	0.26	240.30(22.10)
$CaCO_3$ from calcium formate	162	5	860	176.43	0.30	141.00(17.90)
$CaCO_3$ from calcium acetate	114	5	840	178.36	0.29	101.50(17.50)
$CaCO_3$ from calcium propionate	95.5	5	795	174.59	0.35	40.95 (9.53)
$CaCO_3$ from calcium palmitate	36.4	5	780	178.02	0.41	30.73(15.20)
$CaCO_3$ from calcium stearate	31.8	5	760	174.79	1.00	24.35

calcium carbonate formed, the DTG peak- temperature of the decomposition, the reaction order determined by Kissinger's method and the activation energy determined by Freeman and Carroll's method, are summarized in Table 1 for the various organic calcium salts studied. For the sake of comparison the same parameters of reagent grade calcium carbonate are also included in the Table for various sample weights and heating rates.

It can be seen that the decomposition peak temperature of calcium carbonate decreases from 905°C to 760°C when the amount of calcium carbonate is decreased. Nevertheless, the activation energy calculated from the thermal curves fluctuates about a constant value: 175.84 kJ mole^{-1}. This agrees well with those collected by Adonyi [20] from various authors. Five of the 14 published values fall in the 171–180 kJ mole^{-1} range [11,21,22], including an isothermally determined value [11]. However, if the results differing from these values were also taken into account, then the average of the 13 values is 176.85 kJ mole^{-1} [8,21–26]. Among the 14 data there is only one value (397.73 kJ mole^{-1}) which falls outside this range [27]. It has to be noted that these values, which are very close to the theoretical one, could be calculated without the experimental elimination of controlled diffusion.

In addition to these examples, we determined the kinetic parameters of the orthophosphoric acid–pyrophosphoric acid thermal condensation reaction, both isothermally and dynamically (heating rate 10°C min^{-1}, flowing nitrogen atmosphere, platinum crucible with lid, 1-g samples [28]). The two activation energies were in good agreement (43.29 kJ mole^{-1} vs. 40.82 kJ mole^{-1}).

If the reaction order is studied as a function of the heating rate [17], then we find that in the case of solid samples [nickel(II)-hexammin-chloride, polystyrene-divinylbenzene copolymer], the reaction order also changes with the heating rate; it increases with increase in heating rate (both Kissinger's and Horowitz and Metzger's methods). Under the same heating rates the reaction order also changes with the sample weight; the reaction order increases with decreasing sample weight, as is shown by the example of calcium carbonate. The kinetics of trichlorphon decomposition in melt invariably proved to be first order with all three methods.

Relations between the reaction kinetics parameters and the type of thermal process

It could be concluded from the experimental results that changes of the reaction kinetic parameters (activation energy, reaction order) with the heating rate are due, primarily, to diffusion. At low heating rates the decomposition is slow, and so is the diffusion of the gaseous decomposition products. In this case when the weight loss, being theoretically proportional to the quantity of the decomposed material as a function of time, is read from the derivatogram, then a mistake is made because only one part of the gaseous decomposition products can leave the sample (this is read), the other part cannot diffuse, because the small grains of the material have not yet decomposed, so the value read is not proportional to the quantity of the decomposed material. At higher heating rates both the decomposition and the diffusion rates are higher, so the momentary weight loss as determined from the derivatogram is closer to the quantity of gas being evolved at the time. In other words, at high heating rates the diffusion rate is increased to such an extent that the process of transformation is no longer diffusion controlled, rather it follows the actual chemical reaction. Our results indicate that the extent of diffusion is more strongly reflected in the values of reaction order than in the activation energies. Having reached a certain heating rate value the activation energy becomes constant, while the reaction order continues to change [17].

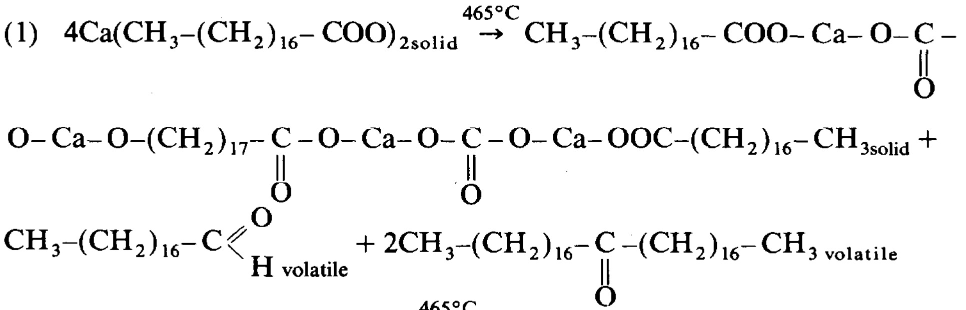
It is the diffusion which makes the reaction order change between zero and unity in the case of the decomposition of solid samples. The reaction order of weight loss accompanied physical processes (evaporation and diffusion) is zero, that of the thermal dissociation is unity [17]. With increasing heating rate and decreasing sample mass the reaction order approaches unity, because the role of diffusion is reduced, and the thermal dissociation is the process determining more and more the reaction order. During the decomposition of solid nickel(II)-hexammin-hydrochloride both solid and gaseous decomposition products are formed [29]. Here, the gaseous products have to pass both the original solid sample and the solid decomposition products, so depending on the degree of diffusion corresponding to the actual heating rate [17], the reaction order changes between 0.2 and 0.6.

The decomposition of calcium carbonate leads to a solid (CaO) and a gaseous (CO_2) product. The smaller the sample mass, the easier the gaseous decomposition products can leave the solid particles. Moreover, the small grains of calcium carbonate formed by the thermal decomposition of calcium stearate are presumably more loosely arranged than those obtained from calcium palmitate, so even though the amount of calcium carbonate is practically identical in both cases (i.e. the sample weight is practically identical), there is a difference in the diffusion rate of the gaseous products. In these cases, depending on the mass, the density of the sample, i.e. the diffusion rate, and the reaction order change between 0.26 and 1.0 (Table 1).

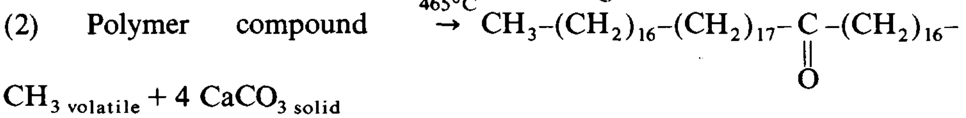
In the case of the solid styrene-divinylbenzene copolymer [30] the decomposition reaction order, depending on the heating rate, changes between 0.5 and 1.0.

The role of diffusion is negligible in the decomposition of molten trichlorphon, so the reaction order does not depend on the heating rate and its value is close to unity. In agreement with this observation, the thermal dissociation of ammonium nitrate in the molten state (in thermokerame or graphite crucible) [17,31] or the orthophosphoric acid–pyrophosphoric acid condensation [28] in the liquid state is also of first-order kinetics.

The reaction order of the catalytic decomposition of ammonium nitrate in a metal crucible was found to be zero [17,31], also a logical observation. The decomposition reaction order of calcium stearate, from which more than two products are formed, was 2 [17,32]. (It should be noted here that the reaction equation in ref. 17, for certain reasons, was published incorrectly.) Two reaction equations describe the process which, according to the derivatogram, proceeds in a single stage [33]



$$(1)\quad 4\mathrm{Ca(CH_3\text{-}(CH_2)_{16}\text{-}COO)_{2solid}} \xrightarrow{465^\circ\mathrm{C}} \mathrm{CH_3\text{-}(CH_2)_{16}\text{-}COO\text{-}Ca\text{-}O\text{-}}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\text{-}\mathrm{O\text{-}Ca\text{-}O\text{-}(CH_2)_{17}\text{-}}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\text{-}\mathrm{O\text{-}Ca\text{-}O\text{-}}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\text{-}\mathrm{O\text{-}Ca\text{-}OOC\text{-}(CH_2)_{16}\text{-}CH_{3solid}} + \mathrm{CH_3\text{-}(CH_2)_{16}\text{-}C}\left\langle\begin{matrix}\mathrm{O}\\ \mathrm{H}\end{matrix}\right._{\text{volatile}} + 2\mathrm{CH_3\text{-}(CH_2)_{16}\text{-}}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\text{-}\mathrm{(CH_2)_{16}\text{-}CH_{3\,volatile}}$$



$$(2)\quad \text{Polymer compound} \xrightarrow{465^\circ\mathrm{C}} \mathrm{CH_3\text{-}(CH_2)_{16}\text{-}(CH_2)_{17}\text{-}}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\text{-}\mathrm{(CH_2)_{16}\text{-}CH_{3\,volatile}} + 4\,\mathrm{CaCO_{3\,solid}}$$

Reaction-order values calculated from the thermal curves are reasonable and they are in agreement with those already known.

(1) The reaction order of evaporation is zero.

(2) If there is thermal dissociation and the role of diffusion is negligible, such as in the thermal decomposition of trichlorphon and ammonium nitrate in melt, and in that of phosphoric acid in solution, then the reaction order is unity.

(3) If diffusion plays an important role, because the gaseous decomposition products have to leave through solid particles, then the reaction order is between zero and unity.

(4) The reaction order of catalytic reactions is zero.

(5) When there are more than two decomposition products (solid + volatile), then the reaction order is larger than unity.

There also exist certain relationships between the activation energy and the type of reaction.

(1) Polymer ageing influences its decomposition temperature and activation energy: both the thermal stability and decomposition activation energy of styrene-divinyl-benzene copolymer decreased after ageing of 4 years [17].

(2) The activation energy of the catalytic decomposition of ammonium nitrate is much smaller than that of the simple thermal dissociation [17,31]. It is also the catalytic effect which lowers the activation energy of the thermal decomposition of nickel(II)-hexammin-chloride observed when it is heated in a platinum crucible and in air atmosphere [3,4], from its high value observed in flowing nitrogen atmosphere [17].

Calculation of the half-life time

If the activation energy (E^x), reaction order (n) and peak temperature (T_s) values are known, then, following the demonstration of Horowitz and Metzger [9], the half-life time of decomposition ($\tau_{1/2}$) can be calculated at various temperatures. If $T = T_s$, i.e. the selected temperature and the peak temperature are equal, then the frequency factor (Z) can be calculated as

$$Z = \frac{\phi E^x \exp(E^x/RT_s)}{RT_s^2} \tag{2}$$

where ϕ is the heating rate (°C min^{-1}), and R is the gas constant (8.309×10^{-3} kJ).

If Z is substituted into the Arrhenius equation of the rate constant, k

$$k = Z \exp(-E^x/RT) \tag{3}$$

then, k becomes

$$k = \frac{\phi \dfrac{E^x}{RT_s^2} \exp(E^x/RT_s)}{\exp \dfrac{E^x}{RT}} \tag{4}$$

It is known that for first-order reactions the half-life time of decomposition can be calculated from the rate constant

$$\tau_{1/2} = \frac{\ln 2}{k} \tag{5}$$

If eqn. (4) is substituted into eqn. (5) and the activation energy, reaction order and peak temperature values are known, then the half-life time can be calculated.

When the reaction order is not unity, then the half-life time can be calculated as

$$\tau_{1/2} = \frac{(2^{n-1} - 1)}{C_0^{n-1}(n-1)k} \tag{6}$$

where C_0 is the initial concentration of the material.

The half-life time of calcium carbonate held at 700°C was calculated from the data shown in Table 1. It has to be noted that in those calculations when $n \neq 1$ the initial concentration of the material was taken as unity, because pure calcium carbonate was always examined. The results are shown in Table 1. It can be seen that half-life time changes with the sample mass. To obtain the true half-life time of thermal dissociation we have to take into consideration the sample mass as the concentration. In our experience the half-life time values become nearly the same when a multiplication term, $C_0^{10C_0(1-n)}$ is applied, where C_0 is the sample mass in g. (Other empirical

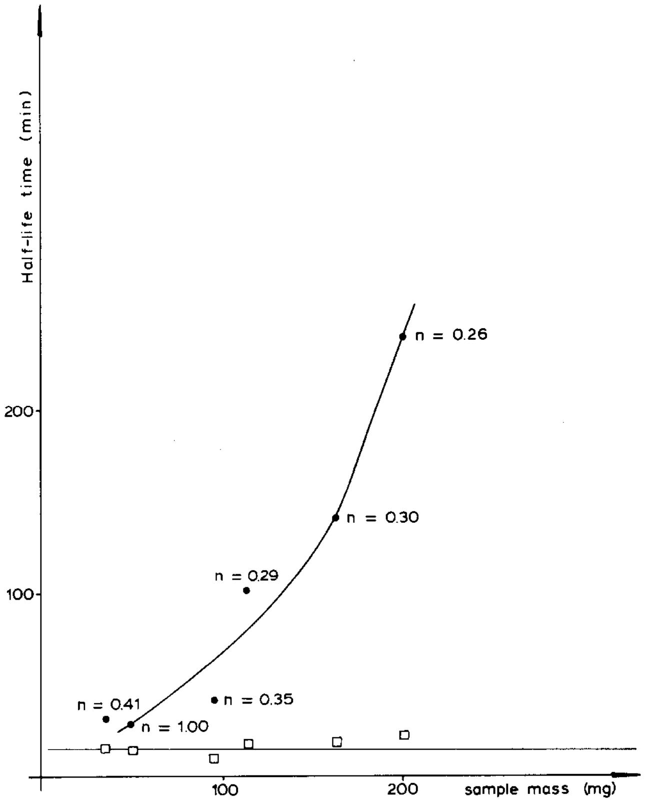


Fig. 1. Half-life time as a function of the sample mass in the case of calcium carbonate. C_0 = Initial concentration (sample mass). ●, $C_0 = 1$; □, $C_0 \neq 1$.

factors were also tried, but they did not give good results.) The data thus obtained are shown in Fig. 1 and Table 1 (in parentheses). The values are consistent within each other, and approach that obtained for $n = 1$. Naturally, the latter is the best estimate of the half-life time of thermal dissociation. It can also be seen in Table 1 that the effect of sample mass, and thus that of the correction term is most important for $n < 0.35$, when the role of diffusion increases with the sample mass. If the effect of sample mass is neglected in those cases, then the delay caused by the large sample mass, i.e. the slow diffusion of the gaseous decomposition products, is reflected in the half-life time values.

Discussion of the experimental results

In summary we can conclude that the parameters of the Arrhenius model are suitable for the derivatogram-based kinetic characterization of the heterogeneous thermal processes. If we wish to determine the kinetic parameters of thermal dissociation as easily as possible, then the experimental conditions have to be selected in such a way that complete dissociation is promoted. Thus, the major goal of the first phase of this study was the determination of those experimental conditions which ensured that thermal dissociation was the major process. At this point the effects of the minor parameters were neglected. The examples shown indicate that such conditions can indeed be realized. Thus, in equilibrium processes the aim is not the achievement of the equilibrium conditions, but rather the complete shifting of the reaction into the desired direction.

This can be assured by small sample mass, suction of the gas phase, high flow rate of the purging nitrogen, in the case of materials sensitive to air, and high heating rates (10°C min^{-1}). It seems probable that the use of labyrinth crucibles does not help the shift of the equilibrium. The conclusion of certain researchers that the shapes of the thermal curves are more characteristic of the experimental conditions than of the transformation studied is not correct. The shapes of the curves must be characteristic of the transformation, but they are influenced by the experimental conditions. Since the transformation proceeds differently under the various conditions (the extent of diffusion, secondary reaction, adsorption, desorption, nucleation, etc.), then the shapes of the curves change, and this is also reflected in the reaction kinetic parameters derived from the curves. With knowledge of many of these parameters, a model of the complex thermal decomposition processes can be constructed. In view of the relationships which exist among the thermal processes and the kinetic parameters, this seems to be a real possibility.

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