CORRELATION BETWEEN KINETIC CONSTANTS AND PARAMETERS OF DIFFERENTIAL THERMOGRAVIMETRY, IN THE DECOMPOSITION OF CALCIUM CARBONATE

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It is known that in thermoanalytic measurements the quantity of the sample, the rate of heating, the shape of the crucible: generally, the conditions of measurement considerably affect the form of the thermogravimetric (TG) curve, and the temperature at the peaks of differential thermoanalytic (DTA) or differential thermogravimetric (DTG) curves.

According to the studies of PAULIK, PAULIK and ERDEY [1], carried to a high degree of precision and based on substantial experience, the following phenomena are manifest:

1. In measurements carried out on samples placed in the crucible of the apparatus,

a) if the sample is augmented from 40 mg up to 800 mg, the temperature at DTG-peak rises from 800 °C to 920 °C;

b) if the heating rate is increased from 1 °C · min^{-1} to 10 °C · min^{-1}, the temperature at DTG-peak rises from 750 °C to 920 °C;

c) if in a mixture of calcium carbonate and an inert substance the ratio of the latter is reduced from 96 per cent to nil, the temperature at the peak rises from 780 °C to 920 °C.

2. In measurements carried out on samples placed on the polyplate sample-holder proposed by PAULIK, PAULIK and ERDEY [1], they have stated that,

a) if the sample is augmented from 10 mg up to 200, mg the temperature at DTG-peak rises from 660 °C to 730 °C;

b) if the heating rate is increased from 1 °C · min^{-1} to 10 °C · min^{-1}, the temperature at DTG-peak rises from 660 °C to 730 °C;

c) if the ratio of the inert substance is reduced from 96 per cent to nil, the temperature at DTG-peak rises from 670 °C to 730 °C.

The authors cited have found that the variation of the temperature at DTG-peak (derivative of the TG-curve) is a function of partial pressure of carbon dioxide, itself a function of the conditions of measurement, and that by the use of the polyplate sample-holder results close to those obtainable in measurements in vacuo can be arrived at. PAULIK, PAULIK and

ERDEY [1] tried to counterbalance the effect exerted by the conditions of measurement by an increase of the number of data obtainable simultaneously i.e. by measurement, at the same time, of DTA, DTG and dilatometric data, apart from the standardization of the method. In connexion with the study of the hydration products of cements, PETZOLD and GÖHLERT [2] have broached the subject of such a standardization. In general it may be said that without the knowledge of the exact circumstances of measurement thermal decomposition is not accurately defined by the temperatures at DTA or DTG peaks, respectively. The question might be raised whether kinetic constants are suitable for the definition of thermal processes, respectively, how variations of the conditions of measurement affect the kinetic constants of a thermal decomposition.

Several authors have made attempts at some calculations from data furnished by thermoanalyses of kinetic constants viz. of the order of reaction and of activation energies, using calcium carbonate as the model substance.

Data, as collected and shown in *Table 1*, demonstrate that though the experiments themselves were carried out under quite varied circumstances the kinetic data calculated by the several authors were around certain values. This seems to suggest that kinetic constants are more suitable for the characterization of thermal processes than are temperature values that appertain to peaks. On the other hand, the discrepancies seem to suggest that the constants obtained by calculation are sensitive to circumstances that prevailed at measurement. Unfortunately, the data given are incomplete in many cases, therefore no unequivocal correlation between divergence of kinetic constants

Table 1

Reference	Order of reaction	Activation energy, Kcal · mole^{-1}	Supplementary information
HUTTIG KAPPAL [3]	0...1	49	Isothermal
VALLET, RICHTER [4]	0.2...0.53		Isothermal
FREEMAN, CARROLL [5]	0.4	39	DTG (TG)
BRITTON, GREGG, WINSOR [6]	0.74	41.6	DTA (vacuum, grain size 1 mm)
id.	0.3	35...42	air
BISCHOFF [7]		47	DTA
SLONIM [8]	1	41...44	
SPLICHEL, SKRAMOVSKY, GOLL [10]	0.3	37...39	
KISSINGER [9]	0.32	43.7	DTA
id.	0.22	42.9	Isothermal
MASKILL, TURNER [11]	1	95	
ZAWADSKI, BRETSZNAJDER [12]		48	

and conditions of measurement could be established on the basis of data published in the literature.

Records published by PAULIK, PAULIK and ERDEY [1] too are deficient in some data needed for calculation, therefore we tried to repeat the thermal measurements in order to study the connexion between kinetic constants and conditions of measurement, and chose calcium carbonate as the model substance. It is known that DTA curves are suitable bases for kinetic calculations, however, in order to arrive at a greater accuracy, in this study only an analysis of results of thermogravimetric measurements is carried out. KREVELEN et al. [13] were the first to utilize thermogravimetric curves in a calculation of kinetic data. Among the methods of calculation that of FREEMAN and CARROLL [5] may be pointed out, with the comment that all the demonstrations known today to be suitable for kinetic calculations are reducible to, or can start with, the derivation that follows, i.e. that these demonstrations are of about the same value.

$$-\frac{dx}{dt} = k(a - x)^{\nu}$$

where $-\frac{dx}{dt}$ is the rate of the change of weight, $(a - x)$ is the mass of substance not decomposed, ν is the order of reaction, k is the Arrhenius constant.

In a calculation, the thermogravimetric (TG) curve is differentiated according to a given method, e.g. graphically. The special advantage of the derivatograph [14] used by us consists therein that it carries out differentiation automatically and in a way suitable for calculations. Thus, for thermal decomposition reactions involving a weight change the differential equation mentioned can be applied directly.

1. Effect of sample mass

In our experiments P. A. grade, precipitated calcium carbonate of 10 to 11 micron particle size was used. Results of measurements as a function of sample mass in the range between 40 mg and 2000 mg are shown in *Fig. 1*.

Depending on sample mass, the temperature at the peak of a DTG curve may be shifted even by 155 °C. Noteworthy is the phenomenon that with a greater sample mass (greater than 1000 mg) the DTG peak appears as a composite peak. When the order of reaction is determined according to the method proposed by FREEMAN and CARROLL [5] *(Fig. 2)*, the log k and $\frac{1}{T}$ function is that shown in *Figs 3, 4, 5, 6* and *7*. Independently of sample mass, order of reaction is 0.25. The function log k and $\frac{1}{T}$ is linear,

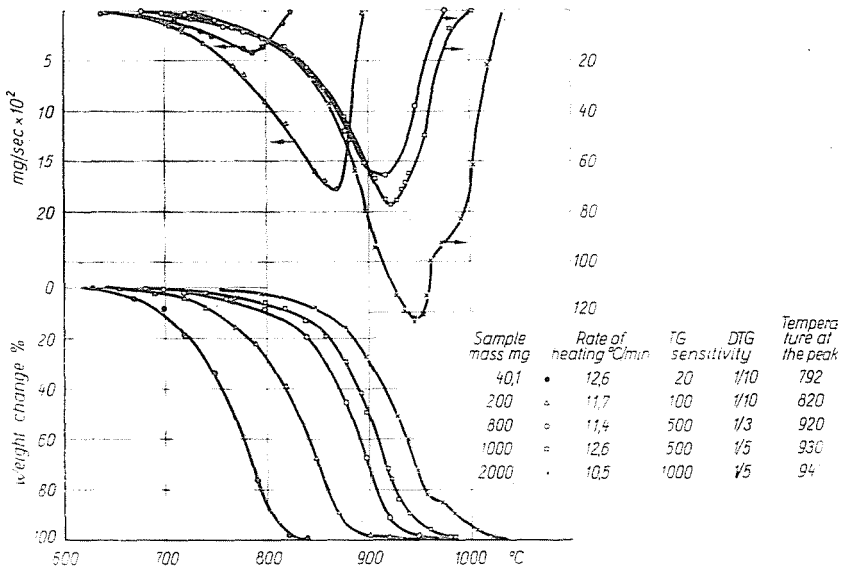


Fig. 1

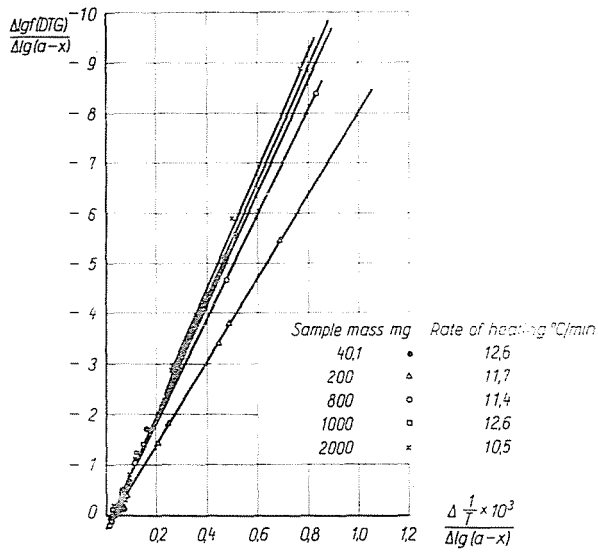


Fig. 2

in a good approximation, for the entire domain of decomposition. The slope of the log k and $\frac{1}{T}$ line changes a little with the change of the mass of the sample, thereby also the calculated values of activation energy change. A characteristic effect in connexion with the kinetic influence exerted by the mass of the sample can be observed on *Fig. 4* (200 mg) where the function

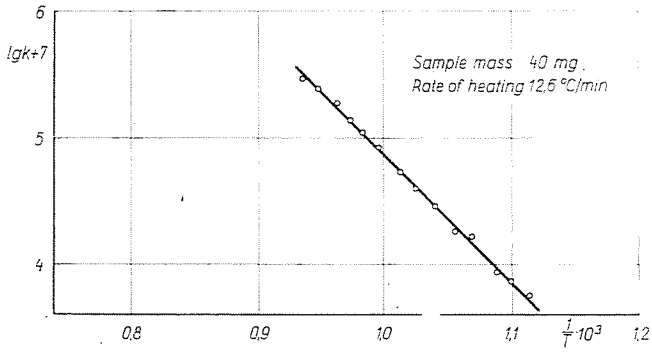


Fig. 3

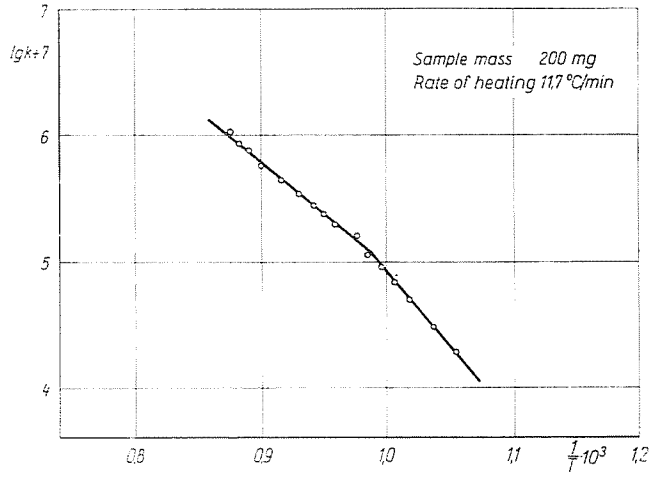
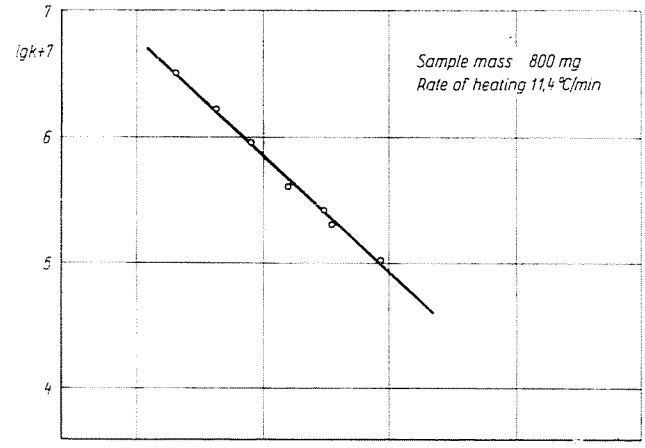


Fig. 4



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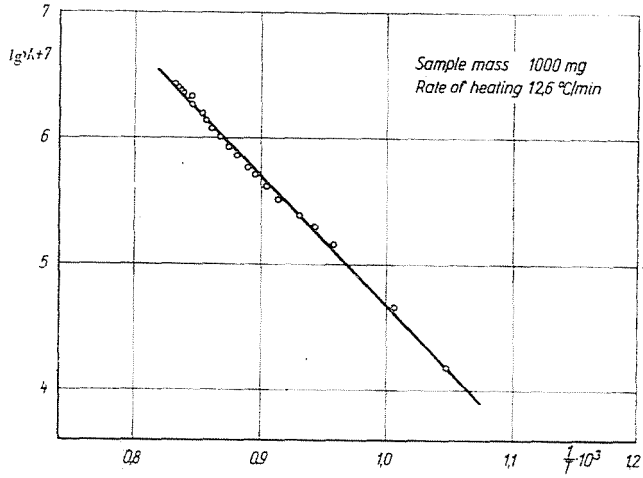

Fig. 6

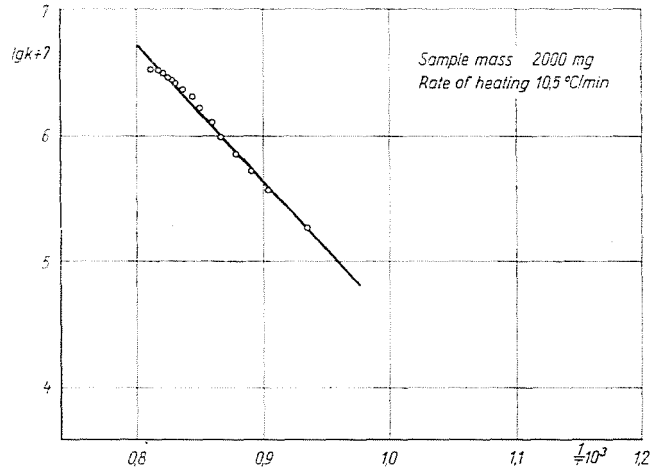

Fig. 7

log k and $\frac{1}{T}$ is composed of two linear sections. That ascribed to low temperatures shows some correspondence to the 40 mg curve, that to higher temperatures shows correspondence to greater sample mass.

Results are collected in *Table 2*. It is to be seen that the mass of the sample affects kinetic constants to a lesser degree than it does at the temperatures in *Fig. 1* that pertain to DTG-peaks. On *Fig. 8*, which contains all the data concerning the mass of samples, an average log k and $\frac{1}{T}$ function can be determined. This was the basis for the

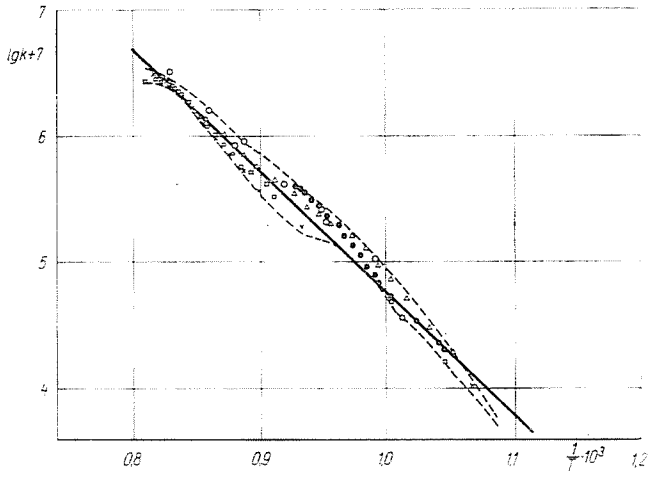

Fig. 8

calculation of the average activation energy shown in *Table 2*. Further study of the asymmetric deviations observable in *Fig. 8* will perhaps help us towards a more thorough interpretation of the effect exerted by the mass of the sample.

Table 2

Crucible	Sample, mg	Rate, °C · min⁻¹	Activation energy, Kcal · mole⁻¹	Temp. range of validity, °C	Activation energy, Kcal · mole⁻¹	Temp. range of validity, °C
Small	40	12.6			46.7	620...790
Small	200	11.7	38.14	737...872	46.6	675...737
Medium	800	11.4	45.9	700...980		
Medium	1000	12.6	46.4	680...945		
Large	2000	10.4	51.6	742...923		
Average, independent of sample mass			45.23	666...947		

2. Effect of the rate of heating

Fig. 9 shows derivatograms recorded for rates of heating of 3.7, 8.2, and 11.7 °C · min^{-1}, respectively. A shift by about 45 °C of the temperatures at DTG peaks is observable. Following the kinetic evaluation of the derivatograms carried out as before, it could be stated that the rate of heating does not affect the order of reaction within the interval studied: this value is 0.25

in all three instances. The log k and $\frac{1}{T}$ function is shown in *Fig. 10*, values of activation energies are collected in *Table 3*.

Table 3

Rate of heating, °C · min⁻¹	Temp. at transition point, °C	Activation energy, Kcal · mole⁻¹	Temp. range, °C	Activation energy, Kcal · mole⁻¹	Temp. range, °C
11.7	747	55.5	647...747	36.3	747...867
8.2	735	56.3	677...735	40.5	735...747
3.7	696	56.8	655...693	43.3	693...827

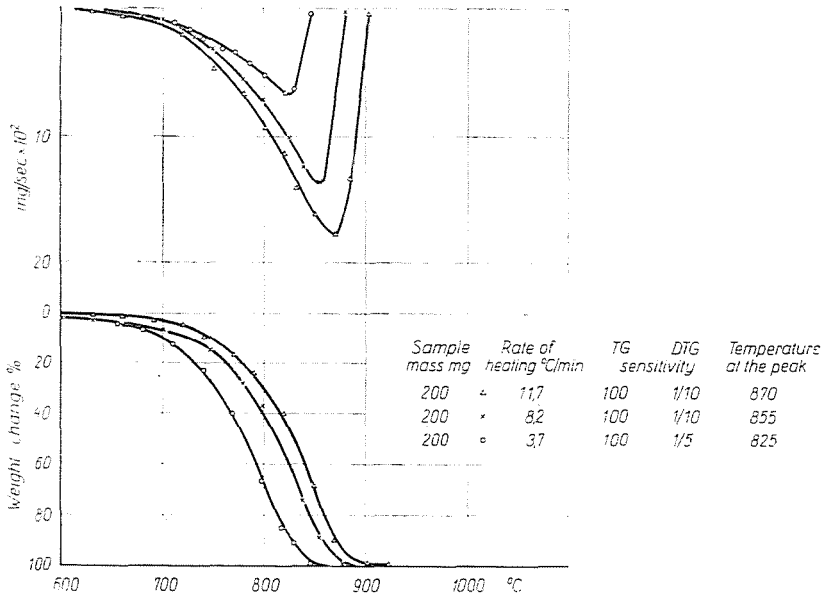

Fig. 9

On the log k and $\frac{1}{T}$ diagram the temperature at transition point changes with a change of the rate of heating. When this rate is increased the activation energy decreases in the range of the higher temperatures, it does not change in the range of the lower temperatures, therefore the temperature at transition point is higher.

3. Effect of the shape of the crucible

After the study of the effect of sample mass and rate of heating, respectively, we investigated the effect of some less definite factors the influence

of which might be expected upon diffusion processes. Measurements are grouped as follows.

1. 40 mg samples, 12 °C · min^{-1} heating rate, in a small crucible, and in a large crucible;

2. 200 mg samples, 8 °C · min^{-1} heating rate, in an open crucible, and in a covered crucible;

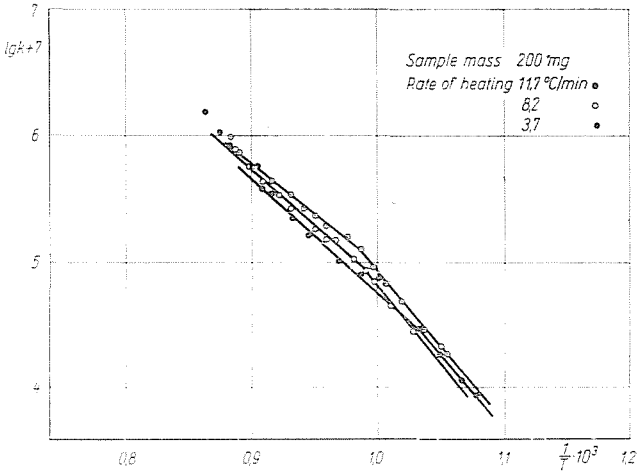

Fig. 10

3. 190 mg samples, 1.3 °C · min^{-1} heating rate, on a polyplate sample-holder proposed by PAULIK, PAULIK and ERDEY [1]*. *Fig. 11* shows the derivatograms. The maximum deviation of the temperatures at DTG-peaks is 212 °C under the conditions chosen. Applying the evaluation method previously described, an order of reaction of 0.25 was found independently of crucible shape. A different value, viz. zero order of reaction was found in the case of the covered crucible. The log k and $\frac{1}{T}$ function is plotted in *Fig. 12*, activation energies are listed in *Table 4*.

Table 4

Crucible	Sample, mg	Heating rate, °C · min^{-1}	Activation energy, Kcal · mole^{-1}	Temp. range, °C	Activation energy, Kcal · mole^{-1}	Temp. range, °C
Small	200	11.7	46.6	674 ... 870		
Small, covered	200	7.5	47.0	698 ... 898		
Polyplate holder	190	1.3	50.8	595 ... 692		
Small	40	12.6	46.7	621 ... 792		
Large	40	11.6	46.9	665 ... 710	38.8	762 ... 800

* These authors were so kind as to oblige with their records of this experiment, we wish to thank them for this co-operation.

As is to be seen, the shape of the crucible is generally of small effect on activation energy. The difference that originates with the crucible being covered with a lid is negligible, but the same k rate constant is reached at a temperature higher by about 60 °C. It is noteworthy that if a polyplate sample-holder is used the rate constant that pertains to a given temperature is about ten times as high as the rate constant measured with a sample in a conventional crucible.

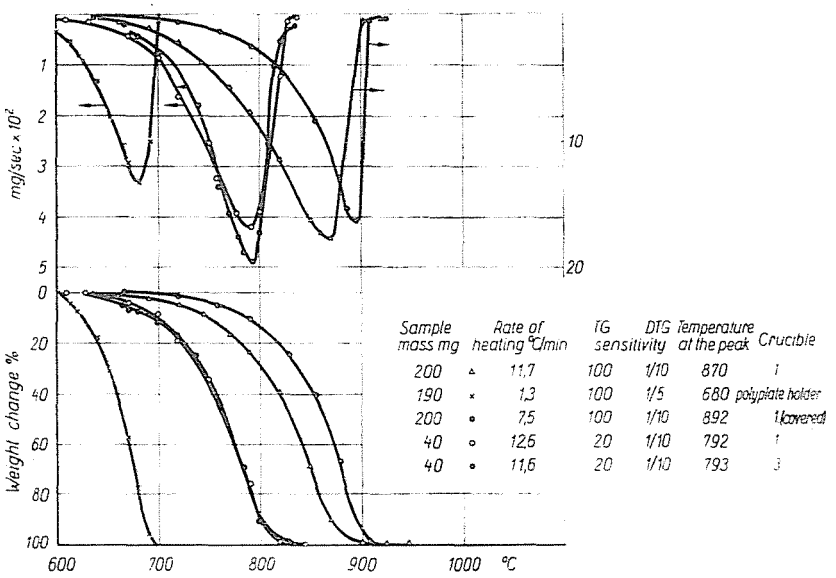

Fig. 11

The result of a measurement on a 40 mg sample in a large crucible allows the conclusion to be drawn that the diffusion from and into the crucible of the gas layer above the substance exposed to the effect of heat, can be of significant influence.

In spite of the decreased thickness of the layer of the substance, the activation energy of 64.9 Kcal · mole^{-1} in the domain between 727 and 762 °C was unusually high. From the log k and $\frac{1}{T}$ function of measurements on 40 mg samples in a large crucible the activation energy was 46.9 Kcal · mole^{-1} in the 665 to 710 °C, 64.9 Kcal · mole^{-1} in the 727 to 762 °C, and 38.78 Kcal · mole^{-1} in the 762 to 800 °C range.

The deviations between this curve and the data taken from the literature in *Fig. 8* can be explained, on the one hand, that in their calculations some authors started from a not sufficiently generalized section, perhaps from one distinguished by special conditions of measurement, of the log k and

$\frac{1}{T}$ function, on the other hand, that under the influence of diffusion processes activation energy fluctuates between certain limits according to conditions of measurement. For the characterization of the thermal process, besides the calculation of the order of reaction and of activation energy the determination of the temperature limits within which these are valid is advisable, or of the log k and $\frac{1}{T}$ function, which is the basis of a deeper insight into the processes.

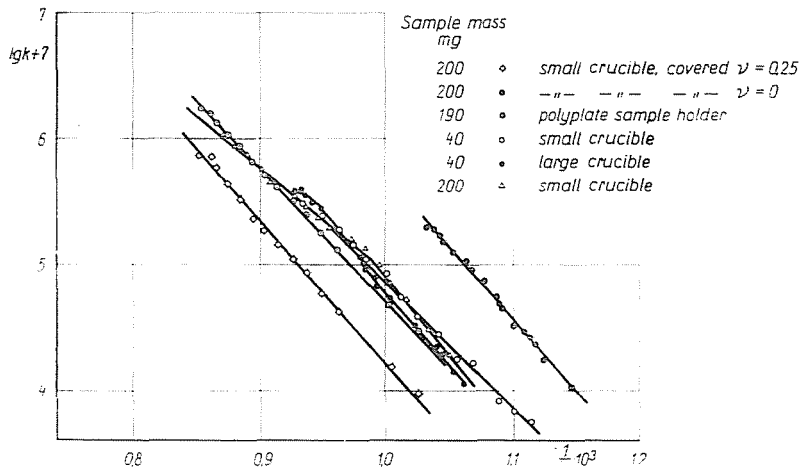

Fig. 12

In summarizing the results we might state that the values of kinetic constants calculable from thermogravimetric data are much less affected by the conditions of measurement than are the shapes of the TG, or of the DTG curves, and the temperatures at the peak of the DTG curves. Therefore order of reaction, activation energy and the log k and $\frac{1}{T}$ function simultaneously utilized seem to be adequate for the characterization of thermal processes. When kinetic constants are known, the identification and the interpretation of thermal processes become easier.

Summary

Data obtained in thermic measurements, the respective shapes of TG, DTG and DTA curves, the temperatures at peaks are strongly affected by the conditions of measurement, the mass of the sample, the rate of heating, the shape of crucibles, etc. Using calcium carbonate as the model substance, a kinetic analysis with the aid of the conventional differential equation has shown that kinetic constants, order of reaction, activation energy are affected in a lesser degree by the conditions of measurement and are, therefore, better suited for a characterization of thermal processes than is a statement of e.g. the temperature at the peak of a DTG curve. A study of the correlation between conditions of measurement and kinetic

constants facilitates the interpretation of thermal processes. From this point of view the knowledge of the function rate constant vs. temperature offers the most information and without this the activation energy is not of full value in the characterization of a thermal process.

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