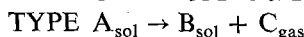


DETERMINATION OF THE KINETIC CONSTANTS
OF ENDOTHERMIC DECOMPOSITIONS OF THE



KINETICS OF SIMULTANEOUS REACTIONS

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The present work describes the endothermic decompositions of calcium carbonate and nickel carbonate, recorded on a MOM derivatograph in the non-isothermal mode at different heating rates. The possibility and advantages of determining the kinetic parameters E , Z , and n for reactions proceeding in one step, as well as the detection of simultaneous (parallel or concurrent) reactions in the decomposition process, are discussed.

The results obtained permit the conclusion that the thermal decomposition of calcite occurs in one step. In this case, the kinetic equation has the following form:

$$\lg \left[\frac{d\alpha}{(1-\alpha)^n} \right] = \lg \frac{Z}{q} - \frac{E}{2.3R} \cdot \frac{1}{T}$$

where $f(\alpha) = (1-\alpha)^n$, $n = 0.3$, and $E = 176.8$ kJ/mol.

In the case of nickel carbonate the results of treating the experimental data have been obtained only in the graphical form. From the shape of the curves obtained, it is clearly seen that the decomposition of nickel carbonate in open air proceeds in several steps (i.e. several simultaneous reactions take place), which cannot be described by the equations for a one-step reaction.

The non-isothermal kinetics of endothermic reactions of decomposition in powdered solids of the type $A_{\text{sol}} \rightarrow B_{\text{sol}} + C_{\text{gas}}$ depends mainly on the extent to which the rate of heat and mass transfer in the sample during the experiments is higher than the rate of chemical reaction at the solid interface (A_{sol}).

Investigation of the kinetics of the chemical reaction proper is usually of principal practical interest. Therefore, in the case of investigations of this kind, especially in the non-isothermal heating mode, the essential experimental problem is reduced to separation of the chemical reaction from the quicker heat and mass transfer taking place with the substance under study in a crucible.

For the experiments, use was made of a thermal balance or derivatograph. This is very suitable since it ensures strictly linear or hyperbolic heating [1-3] with measurement of the temperature of sample decomposition in a special crucible (a plate).

The rapid removal of the gas evolved during the reaction is achieved by spreading finely-ground substance in a thin layer onto the plates of a special multistage

platinum crucible; this eliminates the phenomenon of diffusion inhibition due to the gaseous phase. This, in turn, provides a possibility of calculating from the experimental data the kinetic parameters of a slower chemical reaction, for example a decomposition reaction, which is recorded in the form of a TG curve and a peak in a DTG curve (one-step reaction). The kinetic parameters for the one-step reaction are calculated via the known differential equation:

$$\ln \frac{d\alpha}{(1-\alpha)^n} = \ln \frac{Z}{q} - \frac{E}{R} \cdot \frac{1}{T}. \quad (1)$$

The activation energy E and pre-exponential Z are usually determined graphically. However, in this case the form of the function $(1-\alpha)^n$ must be preset, i.e. the value of n should be determined. Different experimental methods for the determination of n are given in [4–6]. Very often, the form of non-isothermal DTG curves points to the presence of more than one reaction (step) in the decomposition process. If such reactions (steps) are sufficiently well differentiated with regard to time, then in a derivatogram for a common TG curve there are several distinct and independent DTG peaks. This means that one reaction is completed before the next begins, i.e. have to deal with different independent reactions, and each of them may be described by the usual methods and equations for calculating the kinetic values in one-step reactions. However, in practice many decomposition reactions of the type $A_{\text{sol}} \rightarrow B_{\text{sol}} + C_{\text{gas}}$ occur not in one step, but in several parallel or consecutive reactions (steps) that are superimposed on one another and cannot be detected from the forms of the TG and DTG curves. There is no physical sense in calculating the kinetic parameters (E , w , n) in accordance with the experimental data from such an overall TG (DTG) curve. The results thus obtained would be average, misleading values for the decomposition process as a whole. In such cases, when one reaction is superimposed on others, during the decomposition of the substance under study, the detection and, all the more, the isolation for kinetic calculations of consecutive and parallel reactions from only one TG (DTG) curve presents great difficulties. In the literature a possibility is indicated of identifying a two-step reaction of decomposition of solids from only one TG (DTG) curve plotted in a slow linear heating mode (about 2 deg/min) for a very small sample (about 10 mg) in a high vacuum of 10^{-5} to 10^{-6} mm Hg [7, 8]. This technique, however, requires many parallel experiments, with very accurate calculation by statistical and mathematical methods of the second derivative (DDTG) from the experimentally plotted TG (DTG) curves. Such calculations result in very large errors, caused by the scatter of the experimental points of the TG (DTG) curves. With the aim of the more unambiguous calculation of the kinetic parameters of one-step reactions, some authors measure the experimental data from several TG curves plotted at different heating rates [9–12]. A method was proposed in which, for several DTA curves, the kinetic constants for the two-step thermal decompositions of a number of compounds were calculated with the use of the heat evolution value [13].

As will be shown below, by using several TG and DTG curves plotted for the same compound on a derivatograph at different heating rates, we have attempted to reveal, the presence of one or several steps (reactions) in the process under consideration. We have also attempted to establish a possibility of determining separately the activation energy E for each decomposition degree α , without presetting the function $f(\alpha) = (1 - \alpha)^n$, i.e. n [14].

Experimental

A MOM derivatograph was used for the experiments. Crystalline calcite (CaCO_3) and nickel carbonate (NiCO_3) were chosen as the compounds to be investigated. A calcite sample of 100 mg, with a particle size of about 0.1 mm, was heated in a platinum plate-shaped crucible in air. Thus, comparatively large samples can be used: this enhances the weighing accuracy and simultaneously obviates the temperature drop in the thin mass of sample where the temperature is measured. During heating, the conditions of the experiments should be previously adjusted in such a manner that the measurements of temperature and weight are accurate, as otherwise large errors may be introduced into the determination of the primary experimental data and the subsequent calculations of the kinetic parameters [15]. The rate of temperature increase in a sample was maintained strictly constant during the entire experiment; the following rates were applied: 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 deg/min.

Figure 1 presents the experimental TG and DTG curves for the decomposition of calcite (CaCO_3), plotted at different rates of temperature rise.

Figure 2 presents the same curves of decomposition of calcite in the form more convenient for our kinetic calculations, i.e. depending on the transformation depth α .

Transformation of the initial experimental value of the instantaneous decomposition rate taken from the derivatogram, i.e. $\frac{dl}{dt} \text{ deg}^{-1}$ into $\frac{dl}{dt} \text{ sec}^{-1}$ is effected in accordance with the formula $\frac{d\alpha}{dt} = q \cdot \frac{d\alpha}{dt}$, where $q = \frac{T}{t}$.

Calculation of E and Z was carried out with the aid of Eq. (1) which after transformation gives the working logarithmic form:

$$\ln \left[\frac{d\alpha}{dt} \cdot q \right] = \ln [Z \cdot f(\alpha)] - \frac{E}{R} \cdot \frac{1}{T}, \text{ where } q = \frac{dT}{dt}$$

$$\lg \left[\frac{d\alpha}{dt} \right] = \lg [Z \cdot f(\alpha)] - \frac{E}{2.3R} \cdot \frac{1}{T}. \quad (2)$$

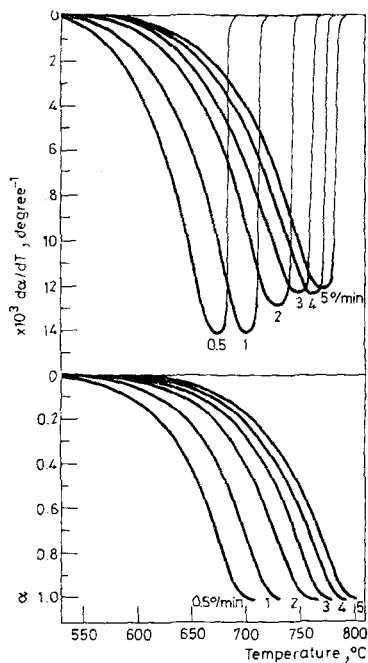


Fig. 1. Kinetic curves of decomposition of calcite sample plotted at different heating rates

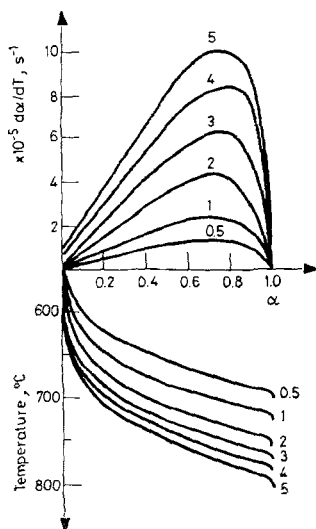


Fig. 2. Kinetic curves of decomposition of calcite, depending on the transformation depth α

Assuming any arbitrarily chosen transformation depth (Fig. 2) as a constant value, linear graphs are plotted in coordinates $\ln \frac{d\alpha}{dt}$ vs. $\frac{1}{T}$ (K^{-1}) from a series of Eq. (2) calculated for the curves obtained at different heating rates. The slopes of the straight lines thus obtained allow calculation of the activation energy E and

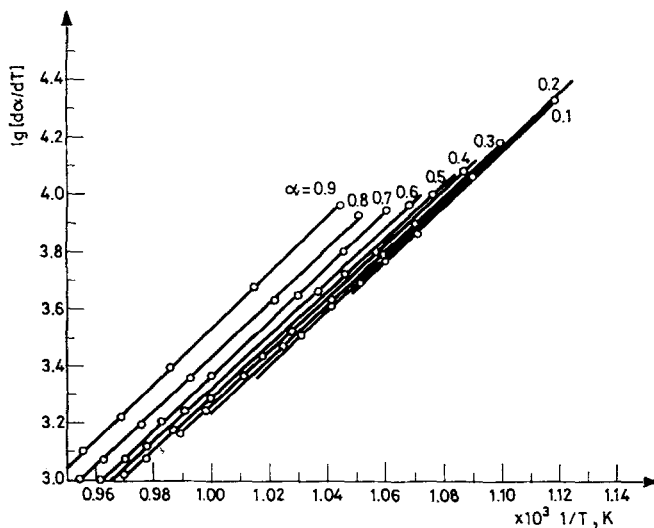


Fig. 3. Graphical determination of activation energy for decomposition of calcite at different values of α

the intercepts on the ordinate give the value of $\ln [Z \cdot f(\alpha)]$ for each α . The parallel arrangement of the straight lines in Fig. 3 is indicative of the constant value of the activation energy for the transformation depths under consideration.

The activation energy was also computed by the least-square method in accordance with the equation $y = a + bx$, where:

$$y = \lg \frac{d\alpha}{dt}$$

$$a = \lg [Z \cdot f(\alpha)]$$

$$b = \frac{E}{2.3R}$$

$$x = \frac{1}{T} (K^{-1}) \cdot 10^{-3}.$$

The values of y and x were taken from Fig. 2, and the values of a and b were calculated for each of them. The value of b enabled calculation for each α of the

value of E in accordance with the formula $E = b \cdot 2.3R$, and also the value of $a = wF_1(\alpha)$; this was possible considerably more accurately than graphically (see Table 1).

As appears from Table 1, constant activation energy values are observed within the range of α from 0.3 to 0.7, with an average value $E_{av} = 176.8$ kJ/mol.

Table 1

Determination of K and $\lg [Z \cdot f(\alpha)]$ as functions of α by the least-square method

	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
E kJ/mol	181.4	183.0	175.1	175.9	176.8	177.6	179.3	184.7	187.3
$\lg [Z \cdot f(\alpha)]$	6.30	6.36	5.92	5.94	5.97	5.99	6.04	6.24	6.45

The initial ($\alpha = 0-0.2$) and the final ($\alpha = 0.8-1.0$) periods of decomposition are characterized by somewhat different activation energies. This may be attributed either to an insufficient sensitivity of the thermal balance of the derivatograph or to the mechanism of decomposition [16, 17].

The least-square computation method was applied to the linear dependence

$$\lg [Z \cdot f(\alpha)] = \lg Z + n \cdot \lg (1 - \alpha) \quad (3)$$

and yielded the values $Z = 10^{-6} \text{ s}^{-1}$ and $n = 0.3$.

Thus, for the decomposition of calcite the average values have been established as $E = 176.8$ kJ/mol, $Z = 10^{-6} \text{ s}^{-1}$ and $n = 0.3$ within the decomposition range $\alpha = 0.3-0.7$. It is seen that to determine the values of E and Z by the above calculation method, it is not required to preset the form of the function $f(\alpha) = (1 - \alpha)^n$, i.e. the value of n . The kinetic parameters (E , Z , n) obtained for the decomposition of CaCO_3 correspond to the literature values determined by numerous other methods of isothermal and non-isothermal kinetics. The constant value of E for different transformation degrees α within the entire temperature range indicates that the decomposition of calcite occurs in one step and is described by one formal kinetic equation (1).

The above method may be applied to the decomposition of NiCO_3 . As several authors suppose, the process of thermal decomposition of this compound occurs in several steps [18, 19].

The decomposition of nickel carbonate (Fig. 4) takes place in open air within the temperature range from 300 to 420° in conformity with the reaction:



In general, the TG and DTG curves of decomposition of NiCO_3 are similar in shape to those for CaCO_3 . However, the DTG curve for NiCO_3 reveals a small

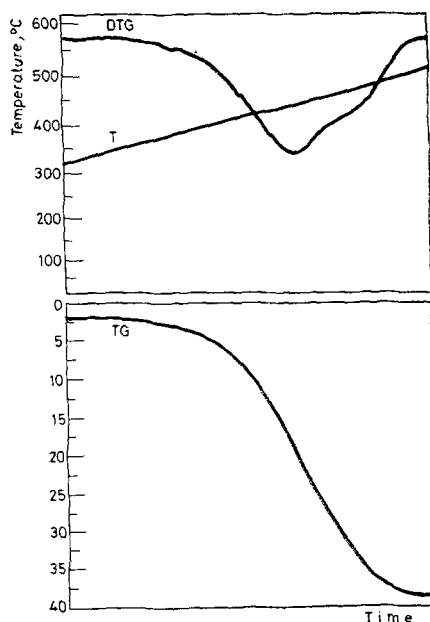


Fig. 4. Kinetic curve of decomposition of NiCO_3 at $q = 8.5^\circ/\text{min}$

bend, which permits the assumption that the process of decomposition of NiCO_3 in open air proceeds in more than one step.

In the experiments use was made of a 100 mg sample of bluish-green crystalline NiCO_3 dried at 120° , whose chemical composition was close to theoretical (about 98.7%); the sample was heated on the plate-shaped crucibles of the derivatograph at the different heating rates of 1, 2, 4, 6 and $10 \text{ deg}/\text{min}$.

Figure 5 presents the shape of curves plotted for kinetic calculations and the transformed TG and DTG curves.

To enhance the accuracy of the calculations, several DTG (TG) curves have been plotted for each heating rate.

From the data of Fig. 5 and from Eq. (2), lines were plotted both graphically and by computation to determine the values of E and $Z \cdot f(\alpha)$ (Fig. 6). However, the plotted lines proved not to be straight and the activation energy E could not be determined with their aid for any decomposition degree, in contrast with the case of the decomposition of CaCO_3 , where the reaction was one-step. From a comparison of the shapes of the curves, it follows that the process of decomposition of NiCO_3 in open air takes place in several steps, that is via several simultaneous reactions. Such a process should be described by a number of kinetic equations.

Comparison of the experimental and calculated data for the decompositions of CaCO_3 and NiCO_3 allows the following conclusion: the derivatographic method involving the plotting of DTG (TG) curves at different heating rates enables one

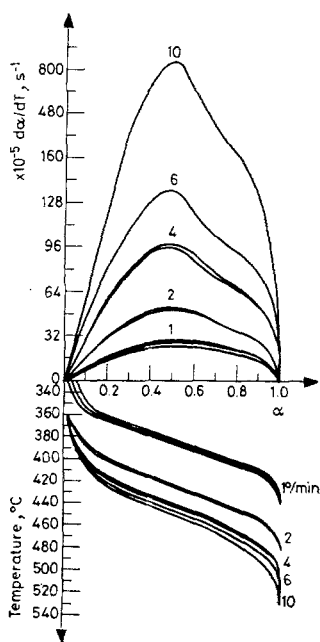


Fig. 5. Kinetic curves of decomposition of NiCO_3 , depending on the transformation depth α

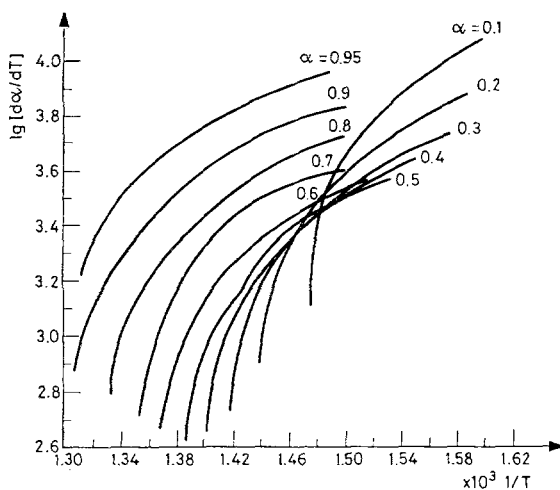


Fig. 6. Graphs for determination of activation energy of NiCO_3 for different values of α

to detect at once the stepwise character (one or a number of steps) of the thermal decomposition of solids.

To establish the kinetic equations of multi-step reactions and to calculate the parameters E and Z , as well as to find the mechanism of the reactions (macrokinet-

ics), it will be necessary to use not only the formal kinetics and the thermogravimetric method, but also other methods, depending on the complexity of the processes, e.g. the electronic paramagnetic method, the nuclear magnetic resonance method, gas chromatography, X-ray structure analysis, scanning electron microscopy, etc.

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ZUSAMMENFASSUNG — Die Arbeit beschreibt die endotherme Zersetzung von Calciumcarbonat und Nickelcarbonat, welche durch einem MOM-Derivatographen in der nicht-isothermen Weise bei verschiedenen Aufheizgeschwindigkeiten registriert wurde. Die Möglichkeit und die Vorteile der Bestimmung der kinetischen Parameter E , Z und n für in einer Stufe ablaufender Reaktionen, sowie der Nachweis simultaner gleichzeitig parallel oder ablaufender Reaktionen im Zersetzungsprozesses, werden erörtert.

Die erhaltenen Ergebnisse gestatten die Schlussfolgerung, dass die thermische Zersetzung von Calcit in einer Stufe erfolgt. In diesem Falle hat die kinetische Gleichung folgende Form:

$$\lg \left[\frac{d\alpha}{(1-\alpha)^n} \right] = \lg \frac{Z}{q} - \frac{E}{2.3R} \cdot \frac{1}{T}$$

für $f(\alpha) = (1 - \alpha)^n$, $n = 0.3$ und $E = 176.8$ kJ/mol.

Резюме — В работе на примере эндотермического разложения карбоната кальция и карбоната никеля, записанных в неизотермическом режиме на дериватографе MOM при разных скоростях нагрева, обсуждается возможность и преимущество определения кинетических

параметров E , Z , n для реакций, идущих в одну стадию, а также обнаружение одновременно идущих (параллельных или конкурирующих) реакций в самом процессе разложения.

Полученные результаты дают возможность заключить, что термический распад кальцита происходит в одну стадию. В этом случае вид кинетического уравнения будет:

$$\lg \left[\frac{d\alpha}{(1-\alpha)^n} \right] = \lg \frac{Z}{q} - \frac{E}{2.3R} \cdot \frac{1}{T}$$

где $f(\alpha) = (1 - \alpha)^n$, $n = 0.3$, $E = 176.8$ кдж/моль,

Для карбоната никеля результаты обработки экспериментальных данных получены только в графическом виде. По внешнему виду полученных кривых ясно видно, что разложение карбоната никеля на воздухе протекает в несколько стадий, т. е. по нескольким одновременно идущим реакциям, и пока не может быть описано уравнениями для одностадийной реакции.