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INVESTIGATION OF THERMAL DECOMPOSITION OF SOLIDS

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Practical aspects of the studies of stages of thermal dissociation of solids, of the kinetics of the stages, and of utilization of general regularities of the process for verification of kinetic studies are discussed.

Introduction

Among chemical processes involving solid reactants one may distinguish as a separate group of reactions the processes of thermal decomposition of the type:

$$A_{solid} \rightarrow B_{solid} + C_{gas}$$

where certain solid substances are transformed into other solid substances with evolution of gaseous products. The processes of thermal dissociation of crystalline substances and mineral materials are usually aimed at either to yield solid products of required chemical compositions, and appropriate activity and usability for further technological applications, or to give suitable gaseous products. Typical examples of such processes include the thermal decomposition of naturally occurring carbonates, e.g. limestone (in the sugar industry and in the production of building materials) chromium, magnesium, strontium, manganese, and other carbonates in the manufacture of oxide catalysts, dissociation of carbonyls and iodides in the production of high purity metals, decomposition of crystal hydrates in the production of surface active agents, etc.

The processes of thermal dissociation may be divided into two groups [1]:

– The first group comprises of the reactions effected as a consequence of rupture of chemical bonds on the anionic sublattice (e.g. thermal dissociation of carbonates), or destroyment of the bonds in the cationic sublattice (as in dehydration of crystal hydrates).

– To the second group belong the reactions based on electron transfer from the anionic to the cationic sublattice. Such a case is observed in the decomposition of double salts, where the rupture of bonds between the sublattices takes place.

There are also reactions which may be classed in either the first or the second group depending on the conditions under which they are carried out. An example of such reactions is the decomposition of ammonium perchlorate, for which the low-temperature reaction (about 230°) consists in electron transfer from the anion to the cation (2nd group), whereas an increase of temperature and a corresponding increase of vibration energy of the lattice elements create a possibility for rupture of the bond between hydrogen and nitrogen in the ammonium cation NH_4 (1st group). As a result proton goes to the perchlorate anion according to equation:

$$NH_4ClO_4 \rightarrow NH_3 + HClO_4$$

The course of thermal decomposition of solids depends of a number of internal and external conditions [2].

The most important internal conditions are:

1) the energy state of starting materials and products of the reaction,

2) mobility of structural elements of the crystal lattice depending on its geometry, type of bonds, charge of lattice elements, etc.,

3) activation energy of the process, which depends on the nature of reactants and the kinetic region,

4) lattice defects,

5) Hedval's effect and occurrence of metastable structural states,

6) similarity of structures of starting materials and products of reaction, etc.

Essential external conditions are:

1) temperature, which determines the mobility of lattice elements and influences the course of the chemical reaction as well as internal and surface diffusions,

2) duration of the process,

3) pressure and composition of the gas phase,

4) catalysts, which may be foreign substances or products of the reaction,

5) particle size of the starting materials, influencing the surface energy and mobility of lattice elements.

Because of the considerable practical and theoretical significance of thermal dissociation processes much attention is given to the investigation of these problems.

The study of thermal dissociation of solids consists usually in:

- the determination of the stages of decomposition and identification of all (if possible) solid and gaseous products of the reaction,
- the determination of the kinetics of each different stage of the decomposition,
- construction of the mathematical model of the process,
- checking the possibility of the occurrence of general regularities in the decomposition of solids in the process.

All these problems will be dealt with in the subsequent chapters of this paper.

Stages of decomposition of solids

An investigation of the thermal decomposition of solids should be started with a determination as accurate as possible of the stages of dissociation of the given compound. The knowledge of all the intermediate stages of thermal dissociation of the given material provides a proper base for kinetic studies. Most kinetic equations are destined for the description of elementary processes. For this reason a precise determination of all the individual stages of the process increases the success of determining the mechanism of all the partial reactions of the compound process.

Complex or nearly complex application of a set of instrumental methods involving thermogravimetry, thermal analysis, mass spectrometry, infrared absorption, and X-ray phase analysis provides very efficient means in the study of thermal dissociation of solid materials. Combined application of these methods allows for a complementary analysis of the processes under study by continuous observation of changes in the composition of both the solid phase and the gaseous phase evolved from the reaction site and reflecting the changes in the composition of the solid reactants,

Investigation of the stages of thermal dissociation of solids include:

- the discrimination of temperature ranges in which individual stages of the decomposition are effected,
- isolation and identification of all (solid and gaseous) intermediate products of decomposition in series corresponding to the rise of temperature,
- identification of the final products of the process studied.

First information on the course of the process of thermal dissociation of a solid substance may be gained from the results of thermogravimetric analysis coupled with thermal analysis, i.e. from the derivatographic analysis. This method enables simultaneous recording of the curves of temperature (T), effects of temperature on the mass of the sample (TG), the rate of mass changes (DTG), and differential thermal analysis (DTA). An essential factor is here a proper selection of the main parameters of the analysis: sample size, kind of atmosphere, and rate of temperature growth during the experiment. The size of samples for study with derivatograph varies from several micrograms to about 10 grams, but a tendency is observed to use rather small samples. The main reason for using small samples is a limited value of their thermal conductivity which involves a temperature gradient between the wall of the crucible and the bulk of the sample. Thus thermal transformations occurring at a definite temperature are not effected simultaneously in the whole volume of the sample, but they proceed gradually along the moving zone of the temperature wave. The greater the sample, the longer is the time necessary for the temperature wave front to cross over the sample. Thus with larger samples the peaks on DTA curves broaden and make it impossible to find the precise transformation temperature.

The peak broadening makes it difficult sometimes to discriminate the peaks corresponding to transformations occurring in short intervals of temperature. These difficulties can be overcome by reducing the size of the sample.

It should also be pointed out that large samples provide worse conditions for diffusion of the gaseous products of reaction. This results in the broadening of peaks on the DTA curve and their shift toward higher temperatures.

The use of very small samples also involve some difficulties, as more sensitive measuring systems are required, and the weighed sample may appear not adequately representative to the material tested.

The composition of the gaseous phase. i.e. the atmosphere in which the decomposition is carried out, is also of great importance in the thermal decomposition of solids. The equilibrium temperature of reversible transformations may depend either on the total pressure in the reaction system or on the partial pressure of one of the components. Thus pressure changes lead to a shift of temperatures at which extrema on DTA and DTG curves occur. Besides, some components of the gas atmosphere may react with the substance studied or with the gaseous products of its decomposition. The result of such processes are additional peaks on the thermal curves. The peaks disappear on changing the composition of the atmosphere. Changes in the pressure of the gas atmosphere may also result in changes of the mechanism of some chemical reactions. From the viewpoint of gas atmosphere in a derivatograph systems it is most advisable to use the atmosphere of a single gas or a high vacuum (10^{-3}–10^{-6} hPa).

Carrying the experiments in vacuum eliminates the possibility of reverse reactions, and thus the results are a direct consequence of thermal dissociation of the substance studied.

An important parameter in thermogravimetry coupled with differential thermal analysis is the heating rate. Besides the shift of the extreme points on the DTG and DTA curves resulting from the temperature dependence of the rate of chemical reactions there is also a noticeable influence of the changes in local atmosphere inside the sample and on its surface.

An increase in the heating rate and the associated increase of the rate of dissociation of the sample material has bearing on the diffusion of gases in the body of the sample and their liberation to the surrounding atmosphere. Usually it is connected with the local increase of partial pressure of the gaseous dissociation products and with a shift of the characteristic peaks on the recorded curves toward higher temperatures. The change in the heating rate leads often to a change in the mechanism of the process and thus it may give an additional information on the course of the thermal dissociation studied. Such an effect of the change in the heating rate may be observed e.g. during the thermal decomposition of basic aluminium-ammonium sulfate in the temperature range of 600–1000° (Fig. 1a, b).

A decrease of the heating rate of the sample makes its possible to obtain DTA and DTG curves of high degree of resolution.

Characteristic transformation temperatures observed under such conditions approach the temperatures of thermodynamic equilibria of the reactions, and the results of thermogravimetric analysis obtained at low heating rates may often be used directly in statistical treatment of the data on the thermal dissociation of solids.

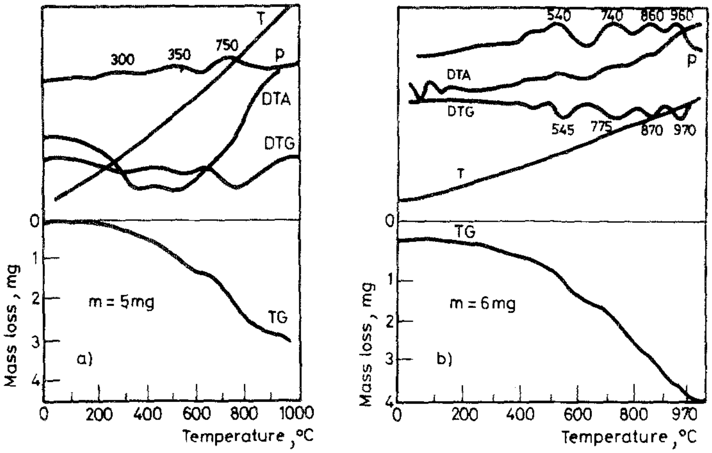

Fig. 1 Thermal curves in vacuum ($p \cong 10^{-6}$ hPa) of basic aluminium-ammonium sulfate. Mettler thermoanalyser, heating rate: a) 2 K/min, b) 10 K/min

An investigation of the thermal dissociation of solids is usually started by taking the thermal curves in air atmosphere (see Fig. 2).

The obtained curves enable the preliminary determination of the main stages of decomposition of the compound and of temperature regions in which the individual stages are effected. Simultaneous interpretation of the TG and DTG curves gives an idea on the magnitude of energy effects of the decomposition reactions and the phase transformations or changes in lattice parameters occurring in the process.

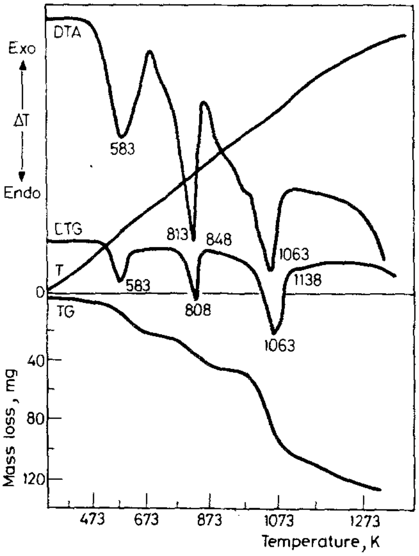

Fig. 2 Thermal curves of basic aluminium-ammonium sultate obtained in air atmosphere [4]

Stoichiometric calculations based on the TG curve enable the preliminary determination of the chemical reactions occurring in the process. This preliminary hypothesis should be then confirmed by means of other methods of investigation enabling the analysis of both the solid and the gaseous products of the decomposition. The identification of solid (both intermediate and final) products of the thermal dissociation may be effected by means of X-ray phase analysis. Different procedures are here applied. Usually the first step is the X-ray analysis of the samples heated for a definite time at temperatures derived from the results of thermogravimetric analysis coupled with differential thermal analysis.

The results of the phase analysis allow to identify the intermediate solid products of the process. X-ray studies may also be performed with the aid of a high-temperature camera. Two ways are applied here: either full analysis of a sample is performed after a required temperature is attained or the intensity changes of selected (known) reflexes are observed and new (expected) reflexes are seeked in order to determine the crystallographic transformation by raising the temperature of the sample with a rate corresponding to the conditions of thermogravimetric analysis.

The results of the crystallographic studies of the intermediate and final products of thermal dissociation by means of X-ray phase analysis are complemented by infrared absorption analysis. This method is usually applied to the study of both the starting materials and the products of their partial decomposition. Infrared absorption studies are particularly useful in cases where it is difficult to identify all the intermediate solid products of decomposition by X-ray diffraction alone. Such cases occur when the internal structure of the analysed substances are of low degree of ordering. It is commonly known that the absence of X-ray reflexes does not necessarily mean the absence of a new phase, since a low degree of ordering of its structure is responsible for the fact that it behaves as an amorphous substance in X-ray diffraction studies. Such a fact is observed in the thermal decomposition of basic aluminium-ammonium sulfate, where X-ray studies do not reveal the presence of compounds containing alumoxane cation in the intermediate products of thermal dissociation (see Table 1), although the presence of such compounds in thermal dissociation processes has been assume by Lorant [5].

The presence of alumoxane cation has been confirmed, however, by means of the infrared absorption spectroscopy [6] (see Fig. 3). Valuable information on gaseous products liberated during thermal decomposition of solids may be obtained by combining derivatographic analysis with mass spectrometry. Such measurements are usually performed in a vacuum thermoanalyser coupled with mass spectrometer. The vacuum thermoanalyser provides a simultaneous recording of the curves of temperature (T), thermogravimetric (DTG), differential thermal analysis (DTA), changes of the total pressure of the gaseous products evolved (P), and of the MTA curve derived from the results of the almost continuous analysis of the composition of evolving gases by means of mass spectrometer. The process is carried out in vacuum which eliminates almost completely the possibility of reverse reactions. Thus the obtained result gives the image of the course of thermal dissociation and contributes

Table 1 X-ray diffraction analyses of basic aluminium-ammonium sulfate and its products

Alunite $K_2O \cdot 3\,Al_2O_3 \cdot 4\,SO_3 \cdot 6\,H_2O$			$3\,Al_2O_3 \cdot 4\,SO_3 \cdot (0\text{-}2)\,H_2O$			Al_2O_3						
standard Mirkin's		starting-sample	standard (ASTM)		sample 893 K	standard Mirkin's γ-Al_2O_3		standard Mirkin's α-Al_2O_3		sample 1173 K	sample 1373 K	
d, Å	*I*	*d*, Å	*d*, Å	*I*	*d*, Å	*d*, Å	*I*	*d*, Å	*I*	*d*, Å	*d*, Å	
5.70	25	5.80	4.53	10	4.65	2.39	19	3.479	72	2.43	2.40	
4.94	50	4.95	3.49	30	3.50	1.975	72	2.552	92	2.07	2.15	
3.49	41	3.50	3.09	100	3.10	1.396	100	2.379	41	1.97	1.99	
2.98	100	3.00	2.47	15	–	–	–	2.085	103	1.40	1.40	
2.29	50	2.32	2.20	10	–	–	–	1.740	83	–	–	
–	–	–	–	–	–	–	–	1.601	42	–	–	

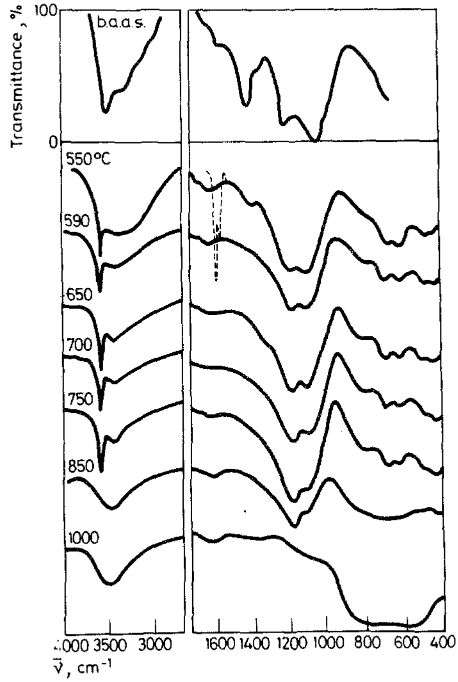

Fig. 3 Infrared spectra of starting material and partly dissociated samples of basic aluminium-ammonium sulfate

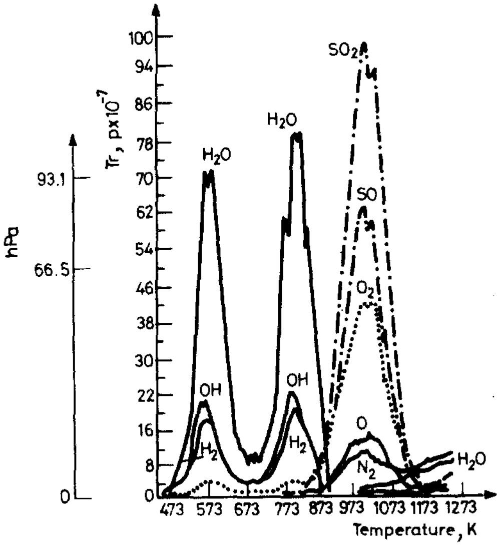

Fig. 4 Effect of temperature (2 K/min) on partial pressure of gaseous products of decomposition of basic aluminium-ammonium sulfate [7]

largely to the recognition of its mechanism. Figure 4 represents an example of the results of thermogravimetric analysis coupled with mass spectrometric analysis of samples of basic aluminium-ammonium sulfate. The measurements were made in Mettler thermoanalyser coupled with quadrupol Balzer's mass spectrometer. The experiments were carried out in vacuum of the order of 10^{-6} hPa with samples of the weight of about 10 mg and a heating rate of 2 K/min. The analysis of the composition of the gas phase has shown that during desulfuration of basic aluminium-potassium sulfate the products of dissociation contain SO_2, SO and O_2, and do not contain SO_3.

Complex interpretation of the results of thermogravimetric, DTA, X-ray diffraction, mass spectrometry, and infrared analyses provides the base for constructing a scheme of the thermal decomposition of the investigated solid substance. An example may be a scheme of thermal dissociation of basic aluminium-ammonium sulfate constructed on the base of results obtained in the complex application of the analytical methods mentioned above [3] (see Table 2).

Kinetics of the thermal dissociation of solids and the mathematical model of the process

Thorough determination of the stages of thermal decomposition of solids enables the investigation of the dissociation rate both in a vacuum and in the atmosphere of the gaseous products. The kinetics of thermal dissociation of solids is studied by both isothermal and non-isothermal methods. The two methods differ widely, but each may be irreplaceable in certain cases. An essential disadvantage of isothermal methods is the lack of the possibility of observing the initial stage of the reaction, where the temperature of the sample remains unsteady. On the other side – the non-isothermal methods require the use of very involved mathematical apparatus for processing the kinetic data obtained from the DTA, DTG, or TG curves.

In most cases the rate of decomposition of solids is studied by isothermal methods. The measurements in selected stages of the process are performed by the gravimetric method under isobaric and isothermal conditions. On the basis of the knowledge of the temperature regions of all dissociation stages of the compound samples are prepared for the study of the reaction rate in individual stages. The measurements are usually carried out either under reduced pressure (10^{-3}–10^{-6} hPa) i.e. eliminating practically any reversible processes, or under the pressure of gaseous reaction products in order to determine the effect of partial pressure on the run of the thermal dissociation process.

The results of such studies are kinetic curves that illustrate the isothermal and isobaric relationship between the transformation degree α and time t.

Mathematical processing of the results obtained in studies of the decomposition rate involves computer techniques and is based on the methods of kinetic analysis. In the latter case the capacity of formal kinetics is used which permits to obtain definite information on the mechanism of the process.

Table 2 Scheme for the thermal dissociation of basic aluminium-ammonium sulfate

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1st stage: partial dehydration of the compound (below 623 K):

$$(NH_4)_2O \cdot 3\,Al_2O_3 \cdot 3\,SO_3(6\text{–}8)\,H_2O = (NH_4)_2O \cdot 3\,Al_2O_3 \cdot 4\,SO_3 \cdot 4\,H_2O + (2\text{–}4)\,H_2O$$

2nd stage: further dehydration and removal of ammonia (within the range 623–873 K):

$$\begin{tikzcd}
 & 3\,Al_2O_3 \cdot 4\,SO_3 + 4\,H_2O + 2\,NH_3 \arrow[d, shift right] \\
(NH_4)_2O \cdot 3\,Al_2O_3 \cdot 4\,SO_3 \cdot 4\,H_2O \arrow[ur, "\text{complete dehydration}"] \arrow[dr, "\text{partial dehydration}"'] & Al_2(SO_4)_3 + \gamma\text{–}Al_2O_3 \text{ (low-temperature modification)} \arrow[u, shift right, "\text{which corresponds to}"'] \\
 & 3\,Al_2O_3 \cdot 4\,SO_3 \cdot H_2O + 4\,H_2O + 2\,NH_3 \arrow[d, phantom, "\text{which corresponds to}"] \\
 & AlH(SO_4)_2 + \gamma\text{–}Al_2O_3 \text{ (low-temperature modification)}
\end{tikzcd}$$

3rd stage: decomposition of sulfate and hydrogen sulfate (above 873 K):

a) decomposition of aluminium sulfate:

$$2\,Al_2(SO_4)_3 \rightarrow 2\,\gamma\text{–}Al_2O_3 + 6\,SO_2 + 3\,O_2$$

b) decomposition of aluminium hydrogen sulfate:

$$\begin{tikzcd}
 & 2\,Al_2(SO_4)_3 + 2\,SO_2 + O_2 + 2\,H_2O, \text{etc.} \\
4\,AlH(SO_4)_2 \arrow[ur] \arrow[dr] & \\
 & 2\,(Al_2O_3 \cdot 3\,SO_4) + 2\,H_2SO_4 \text{ and further decomposition of the sulfate}
\end{tikzcd}$$

c) decomposition of sulfate with formation of intermediates containing Al_2O^{4+} (alumoxane cation)

$$3\,Al_2O_3 \cdot 4\,SO_3 \rightarrow 2\,Al_2O(SO_4)_2 + \gamma\text{–}Al_2O_3$$

$$Al_2O(SO_4)_2 \rightarrow Al_2O(SO_3)_2 + O_2 \text{ (or } 2\,O)$$

$$Al_2O(SO_3)_2 \rightarrow \gamma\text{–}Al_2O_3 + 2\,SO_2 \text{ (or } 2\,SO + O_2)$$

Much care is required in the use of kinetic analysis, as the formal approach does not exclude the possibility of erroneous interpretation of the observed kinetic relationships. Such possibilities arise from the complex nature of thermal dissociation, where no univocal relationship exists between the mechanism of the process and its macrokinetic description.

Thermal dissociation of solids is a complex process with a number of intermediate stages, despite of apparently simple stoichiometric equations applied for its description. The complexity of the process causes that the choice of a kinetic equation adequately approximating the experimental data may not be a criterion of the mechanism followed by the thermal decomposition. The kinetic law is, however, a necessary, although not sufficient condition which should be fulfilled by the supposed mechanism of the process. In practice, analysis of the experimental data is based on several, rarely more than ten equations, if computer calculations are involved in the experimental data processing. The most frequently used kinetic equations have been collected in Table 3. The kinetic curves obtained in experimental studies are further utilized for identification of parameters of the kinetic model of the dissociation of the given compound.

The mathematical processing of each kinetic curve consists in determining the linear regression coefficients for all the equations tested. The calculations follow usually the suitable flodiagram and are performed with the aid of a computer [9].

A criterion for the selection of the most appropriate equation (model) is the value of standard deviation between the calculated and experimental values of $f(\alpha)$. The kinetic parameters, identified by means of the selected equation (Arrhenius activation energy, pre-exponential coefficient), are very useful in recognizing the mechanism of the process. Attempts were also made [9] to correlate the kinetic parameters of the process determined with the use of the isothermal and isobaric methods, with the parameters determined in non-isothermal experiments. Thermogravimetric TG and DTG curves were simulated with the use of kinetic parameters of the decomposition found by the isothermal and isobaric methods. The simulation consisted in numerical integration of the system of equations: equation of the rate of chemical reaction, the form of which depends on the accepted mathematical model of the process, and equation describing the assumed rate of temperature increase in time.

A mathematical model of thermal decomposition of a given compound is constructed for previously determined stages of its dissociation. The starting points of such calculations are the values of the activation energy and pre-exponential coefficient in the Arrhenius equation determined under isothermal and isobaric conditions [9].

It appears that such a simulation of TG and DTG curves is possible for the first and the second stages of dissociation i.e. in cases where the course of the thermal dissociation is identical under both static and dynamic conditions. The course of the TG and DTG curves describing the third stage of decomposition of basic aluminium-ammonium sulfate under conditions of a steady rise of temperature can not be simulated on the basic of kinetic parameters identified in isothermal studies. In construction of a mathematical model of this stage multiple regression method has been applied for determining the kinetic parameters under dynamic conditions. The above considerations lead to the conclusion that works on the construction of a mathematical model of a process (based on kinetic parameters determined under different conditions) requires a thorough knowledge of the dissociation mechanism and possibilities of its changes under the experimental conditions applied.

Table 3 Kinetic equations most frequently applied to describe the kinetics of the thermal dissociation of solids

N°	Equation $t = f(\alpha)$	n	$t = f(\alpha)$
1	Power law α^n	1	α
2		2	α^2
3		$\frac{1}{2}$	$\alpha^{1/2}$
4		$\frac{1}{3}$	$\alpha^{1/3}$
5		$\frac{1}{4}$	$\alpha^{1/4}$
6	Contracting geometry $1 - (1 - \alpha)^{1/n}$	2	$1 - (1 - \alpha)^{1/2}$
7		3	$1 - (1 - \alpha)^{1/3}$
8	Erofeev $[- \ln (1 - \alpha)]^{1/n}$	1	$[- \ln (1 - \alpha)]$
9		$\frac{3}{2}$	$[- \ln (1 - \alpha)]^{2/3}$
10		2	$[- \ln (1 - \alpha)]^{1/2}$
11		3	$[- \ln (1 - \alpha)]^{1/3}$
12		4	$[- \ln (1 - \alpha)]^{1/4}$
13	2D diffusion controlled $(1 - \alpha) \ln (1 - \alpha) + \alpha$	–	$(1 - \alpha) \ln (1 - \alpha) + \alpha$
14	Ginstling–Brounstein $(1 - 2/3\alpha) - (1 - \alpha)^{2/3}$	–	$(1 - 2)\, 3\alpha - (1 - \alpha)^{2/3}$
15	Jander $[1 - (1 - \alpha)^{1/3}]^2$	–	$[1 - (1 - \alpha)^{1/3}]^2$
16	Prout–Tompkins $\ln \frac{\alpha}{1 - \alpha}$	–	$\ln \frac{\alpha}{1 - \alpha}$
17	Second order $\frac{1}{1 - \alpha} - 1$	–	$\frac{1}{1 - \alpha} - 1$
18	Exponential $\ln \alpha$	–	$\ln \alpha$

Regularities in the kinetics of the thermal dissociation of solids

The correctness of the kinetic data gained in a procedure described above should be verified in terms of general regularities of the thermal dissociation of solids. Among the best known and the most frequently observed regularities of the process of thermal dissociation of solids are: the Zawadzki–Bretsznajder relationship, compensation effect, existence of isokinetic temperature, and a specific correlation between the activation energy and supersaturation. All these regularities, which not long ago were only of empirical character, have recently gained theoretical verification [10]. Under conditions of isothermal process an increase of pressure of a gaseous product of the reaction induces a decrease of the rate of thermal decomposition and an increase of the Arrhenius activation energy of the process. The relation $E = f(p)$ has been first observed in 1930 and is known in literature as the Zawadzki–Bretsznajder relationship. Theoretical justification of the Zawadzki–Bretsznajder relationship has been given by Pavluchenko and Prodan [11] as a result of careful analysis of the course of reversible reaction of the type $A_{solid} \rightleftharpoons B_{solid} + C_{gas}$. In order to detect the Zawadzki–Bretsznajder regularity it is necessary to plot the values of rate constant k against the reciprocal temperature for each stage of decomposition of the given compound (see Fig. 5).

The positions of the obtained lines show that with increasing pressure of the gaseous product of the reaction the resulting lines are shifted toward higher temperatures, and their slope with respect to the axis of abscissas, corresponding to the Arrhenius activation energy, rises equally.

The considerable increase of pressure of the gaseous reaction product is not always sufficiently compensated by the increase of temperature. Thus if the effect of tem-

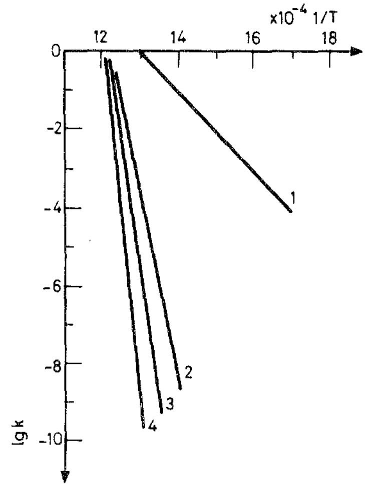

Fig. 5 Relationship between lg k and $1/T$ for the first step of the second stage of decomposition of basic aluminium-potassium sulfate [12]. 1) in vacuum (10^{-3} hPa), 2) $pH_2O = 3.4$ hPa, 3) $pH_2O = 9.8$ hPa, 4) $pH_2O = 18.5$ hPa

perature on the reaction rate is to be described by the Arrhenius equation it appears necessary to change in a definite way also the value of the pre-exponential coefficient A. The nature of the changes of A depending on the changes in E has been described by an empirical equation referred to as a compensation equation

$$\ln A = a + bE$$

where a and b are constants. The values of a and b may be found by determining the regression coefficients for equation $\ln A = f(E)$.

The compensation equation is probably of general character, for the compensation effect has been found to occur in many catalytic reactions, viscosity and diffusion, in studies of electric conductance and electron emission, in biological processes, and in thermal dissociation of many solids.

It has been observed in the studies of decomposition of carbonates [12] and dehydration of crystal hydrates that for a process carried out under different pressures of the gaseous reaction products it is possible to find a temperature β [13], called the isokinetic temperature, at which the numerical values of the reaction rate constants become identical (Fig. 6). The knowledge of the isokinetics temperature β makes it possible to determine the experimental coefficients a and b in the compensation equation (Fig. 6) where

$$a_{\exp} = \log k \quad \text{for} \quad T = \beta$$

and

$$b_{\exp} = \frac{1}{R\beta}$$

The correlation between b_{calc} and $b_{\exp}$, and between a_{calc} and $a_{\exp}$ is not casual, as the terms k, E, T and A are correlated by the Arrhenius equation, and besides, the terms A and E are dually correlated with the terms k and T.

At present it is known [10] that the character of the correlation relationships and their shape should be such as they are, if only the effect of temperature on the process

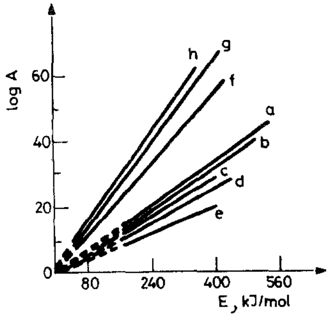

Fig. 6 Compensation relationship. a–e: carbonates of Ca^{2+}, Cd^{2+}, Zn^{2+}, Mn^{2+}, Mg^{2+}; f–h: tripolyphosphates of Na (Na, Ni) and (Na, Mn)

of thermal dissociation may be described by the Arrhenius equation, for the interpretation of the Arrhenius equation as a projection correlation not only enables to state, that the Zawadzki–Bretsznajder relationship, the compensation effect, and the isokinetic temperature are direct consequences of the good interpretation of that equation, but it points also to the existence of other, yet not known (and obviously not studied) relations and their mutual relationships.

Another regularity found experimentally and justified theoretically [13] is concerned with the relationship between activation energy and supersaturation.

Activation energy of thermal dissociation, calculated from reaction rates at different temperatures and at constant supersaturation, is constant and equal to the Arrhenius activation energy of a process carried out under conditions of considerably reduced pressure.

$$E = \text{const.} = E_{\text{vacuum}} \quad \text{for} \quad p(p_0) = \text{const.}$$

where p_0 = equilibrium pressure.

The value of E for $p(p_0)$ = const. may be determined experimentally under conditions of constant supersaturation of the gaseous reaction product or by means of calculations [13] in which use is made of the results of studies on the reaction rate under isothermal and isobaric conditions.

To calculate the degree of supersaturation it is necessary to know the equilibrium pressure of the gaseous reaction product in the given dissociation system. Usually this value is unknown and difficult to determine experimentally because of the occurrence of apparent equilibria. To overcome these difficulties it is possible to make use of a substitute equilibrium pressure p_0^*, which may be found by extrapolation of the relation $r = f(T($ to a temperature at which $r \cong 0$. The existence of correlation between supersaturation and activation energy allows for explanation of i.a. the role of crystallization processes in thermal dissociation reactions. If the experimentally determined value of activation energy is connected with the height of the energy barrier of a chemical reaction or a crystallization process, the invariance of E in a wide range of supersaturations may be accounted for the lack of influence of nucleation and growth of new phase on the run of the process.

The existence of this correlation is also of practical significance. For many reactions of thermal dissociation running in the vicinity of equilibrium or with accumulation of a gaseous reaction product (even under highly reduced pressure) the influence of reverse reaction may not be excluded. In such cases determination of the kinetic parameters may be performed only under conditions of constant supersaturation.

Experimental practice shows that the most profitable way is to combine the two methods for the determination of kinetic parameters, and the coincidence of the obtained results may serve a criterion of the coorectness of the selection of the experimental conditions.

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Zusammenfassung — Die praktischen Aspekte der Untersuchungen über die Stufen der thermischen Dissoziation von Festkörpern und ihrer Kinetik weiterhin über die Anwendungsmöglichkeiten der Regelmässigkeiten der Verifikation der kinetischen Untersuchungen werden erörtert.

Резюме — Обсуждены практические аспекты изучения стадий термической диссоциации твердых тел, кинетики реакционных стадий и применение общих регулярностей процесса для проверки кинетических исследований.