

On methods of studying thermal dissociation of solids

Janusz Pysiak and Barbara Pacewska

*Institute of Chemistry, Płock Branch of the Warsaw University of Technology,
09-400 Płock (Poland)*

(Received 28 January 1992)

INTRODUCTION

Among the primary applications of thermal analysis is its use for the study of reactions in systems containing solid reactants. The domain of applicability is large, therefore, because it comprises such processes as contact catalysis, reactions in solid systems, and heterophase reactions involving solids and liquids. In the group of processes involving solids one can distinguish reactions of thermal decomposition, in which solids undergo transformations resulting in the formation of other solids and evolution of gaseous dissociation products.

The thermal dissociation of crystalline substances and mineral raw materials is usually carried out with the aim of obtaining solid products of the required chemical and phase composition, having adequate activity and usability for subsequent technological applications, or with a view to obtaining suitable gaseous products.

Some examples are: the thermal decomposition of natural carbonates, e.g. limestone (in the sugar industry and in production of building materials), dehydration of crystal hydrates in the manufacture of surface active substances, dissociation of carbonyls and iodides in the preparation of metals of high purity, and the thermal decomposition of chromium, magnesium, strontium, manganese and other carbonates in the production of oxide catalysts and superconducting materials.

The practical utilization of thermal dissociation reactions is among the reasons why a knowledge of the mechanisms and rates of such reactions has become one of the most important tasks of contemporary chemical investigations. The solution of these problems, which is usually difficult and time-consuming, permits intensification of the course of processes important in industrial practice and enables them to be formulated in the correct way.

Correspondence to: J. Pysiak, Institute of Chemistry, Płock Branch of the Warsaw University of Technology, 09-400 Płock, Poland.

The investigations of thermal decomposition of solids are among the most difficult in the chemistry of solid state. These include

- (i) isolation and identification of intermediate (solid and gaseous) and final decompositions products;
- (ii) determination of rate constants;
- (iii) determination of kinetic parameters characterizing the reactions of thermal dissociation, and
- (iv) determination of the effect of state parameters on the course of decomposition.

The course of thermal decomposition depends on many internal and external factors [1]. Among the most important internal factors are

- (i) the energy state of the starting materials and products of the reaction;
- (ii) mobility of structural elements of the space lattice, which depends on the geometry of the lattice, charge of the elements, etc.;
- (iii) activation energy, which depends on the nature of the reacting substances and the region of realization of the process;
- (iv) the dispersion state of the starting materials, which influences the surface energy and the mobility of the lattice elements;
- (v) lattice defects;
- (vi) Hedvall effect and the existence of metastable structural states;
- (vii) structural similarity (or dissimilarity) of the starting materials and products.

To the most important external factors belong

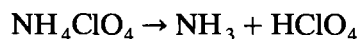
- (i) the temperature, which is decisive for the mobility of lattice elements and influences not only the course of a chemical reaction, but also the space, surface and Knudsen diffusions;
- (ii) the duration of the process (usually long);
- (iii) the pressure and composition of the gas phase;
- (iv) catalysts, the role of which can be played by impurities in the starting materials or by the products of dissociation.

In addition to the factors stated above, the course of thermal decomposition may depend on the nature of decomposition (the chemistry of the reaction), as two types of transformation may be distinguished among the reactions of thermal dissociation [2].

To the first type belong those reactions in which there is a rupture of bonds in the anionic sub-lattice (e.g. dissociation of carbonates) or in the cationic sub-lattice (e.g. dehydration of crystal hydrates).

The other type comprises reactions that consist in electron transfer from the anionic to the cationic sub-lattice. Here we observe the rupture of bonds between the sub-lattices (e.g. decomposition of double salts). There are also reactions which can belong to the first or the second type depending on the conditions of the process. An example may be the decomposition of ammonium perchlorate. At a temperature of about 230°C the reaction proceeds with electron transfer from the anion to the cation

(type II). An increase in the temperature and a corresponding increase of vibrational energy of the lattice elements create a possibility of bond rupture between nitrogen and hydrogen in the NH_4 group (type I) and transfer of a proton to the perchlorate anion:



STUDY OF THE STAGES OF THERMAL DECOMPOSITION

The study of thermal decomposition of solids should begin with as thorough as possible a recognition of the dissociation stages of the given compound. A knowledge of all the intermediate stages enables proper realization of the kinetic studies.

Most kinetic equations describe the so-called elementary processes. Therefore, the more precisely one determines all possible stages of decomposition of a given compound, the greater is the chance of disclosing the mechanism of individual component reactions of the total process.

Actually, studies of this kind involve a complex set of investigation techniques: thermogravimetry, thermal analysis, mass spectrometry, infrared absorption, X-ray phase analysis, and chemical analysis. Such procedures enable a complementary analysis of the process under study by following both the changes in the solid phase and the corresponding changes in the gas phase.

Primary information on the course of thermal dissociation may be obtained from the results of thermogravimetric analysis coupled with thermal analysis carried out by the derivatographic method. An important factor in this analysis is the proper selection of the essential parameters: sample size, composition of atmosphere in the system, and rate of temperature increase.

The size of samples varies from a few milligrams to about 10 g. The main reason for minimizing sample size is limited thermal conductivity, which is responsible for the temperature gradient between the crucible wall and the interior of the sample. The larger the sample, the longer is the time necessary for the temperature wave front to traverse the sample. Hence, in the case of a considerable sample mass the peaks on the DTA curves broaden and make impossible the precise determination of the transformation temperatures. Sometimes the separation of peaks appearing in close succession becomes difficult. Reduction of sample size often affords the possibility of avoiding such problems. In addition, the diffusion inside bulky samples is often limited, thus leading to broadening of peaks on the DTA curve and their shift toward higher temperatures.

The use of very small samples can also lead to particular problems, because smaller samples necessitate higher sensitivity of the measuring

systems, and the composition of the sample may not be representative of the bulk of the material.

A factor of great importance in the transformation discussed here is the composition of the gaseous phase, i.e. the composition of the atmosphere in which the decomposition proceeds. The equilibrium temperature of reversible transformations may depend on the partial pressure of one component or on the total pressure in the reaction system. A change in pressure leads to a shift of temperatures corresponding to peaks on the DTA and DTG curves. Besides, gaseous components of the atmosphere in the system may react with the substance under study or with gaseous products of its decomposition. For this reason the curves obtained may contain peaks that are absent when atmospheres of other composition are applied.

A change of gas pressure can also result in a change of mechanism of some chemical reactions. The best defined atmosphere in a system subjected to derivatographic analysis is obtained in cases where the process is carried out in an atmosphere of a single gas or at high vacuum (10^{-3} to 10^{-6} hPa). Performing reactions in a vacuum practically eliminates the possibility of reverse reactions.

An important parameter in thermogravimetric analysis coupled with thermal analysis is the rate of temperature increase in the sample. In addition to the shift of extrema on the DTA and DTG curves, resulting from the temperature dependence of the rate of chemical analysis, the effects of changes in local atmosphere in the sample and on its surface also become perceptible [3]. DTA and DTG curves recorded at low rates of temperature increase have high resolution, because under such conditions the characteristic temperatures of transformation are closer to the temperature of thermodynamic equilibrium of the reaction. Hence the results of thermogravimetric analysis carried out at slow heating rates may often be utilized directly in static investigation of the thermal dissociation of solids.

The study of the thermal decomposition of solids usually begins with a thermogram recorded in an air atmosphere, which permits one to determine both the essential stages of dissociation of the compound and the temperature regions of individual stages of the decomposition. Stoichiometric calculations based on the TG curve provide a basis for formulating a hypothesis on the course of chemical reactions involved in the process. Confirmation of the hypothesis should be sought with the aid of other methods which enable the analysis of solid and gaseous products of the reaction.

Both intermediate and final products of thermal dissociation may conveniently be identified by X-ray phase analysis. Two types of procedure are applied here. In one of them, "frozen" samples previously heated to the given temperature are subjected to the analysis, and in the other, the formation or disappearance of inflections expected due to a new phase is

looked for in a selected range of temperatures. The latter method requires the use of a high-temperature X-ray camera. The results of such an analysis make it possible to identify the intermediate products of the given reaction. The X-ray studies of changes in crystal structure of the intermediate and final products of reaction are supplemented by spectroscopic studies in the infrared region. These are particularly useful in cases where application of X-ray phase analysis is limited for some reason or other [4,5].

Important information on the gaseous products evolved during thermal decomposition may be gained by subjecting the given substance to derivatographic analysis coupled with mass spectrometry. The result obtained gives a picture of the course of thermal dissociation and facilitates the recognition of the mechanism of the process. Interpretation of mass spectrograms should be made with great care, and should exclude the possibility of imparting the role of gaseous products of thermal dissociation to particles formed in the mass spectrometer.

Joint interpretation of the results obtained by means of thermogravimetric, DTA, X-ray diffraction, mass spectrometric and infrared absorption analyses may serve as a basis for suggesting a scheme of thermal decomposition of the substance [3,6,7]. The scheme should be stoichiometrically correct and should be subjected to careful thermodynamic verification. Thermodynamic analysis of all stages of the process permits exclusion of the possibility of some reactions under the given conditions, and makes it possible to confirm the correctness of the determined composition of the solid and gaseous phases formed in the analysed system.

KINETICS OF THERMAL DECOMPOSITION. MATHEMATICAL MODEL

Determination of the stages of thermal decomposition enables the study of the rate of dissociation in vacuum and in the atmosphere of gaseous reaction products. The kinetics of thermal dissociation may be studied by either isothermal or non-isothermal methods. In the isothermal methods, the measurements concerning individual reaction stages are performed gravimetrically under isobaric and isothermal conditions. The process is usually carried out under reduced pressure (10^{-3} to 10^{-6} hPa) or under the pressure of the gaseous reaction products in order to discover the effect of partial pressure on its course. As a result, one obtains kinetic curves, which represent the relationship between the isothermal and isobaric transformation degree (α) and time (t). The results of decomposition rate measurements are treated by the methods of kinetic analysis, and calculations are performed by computer techniques.

The kinetic analysis makes use of relationships of formal kinetics which provide definite information on the mechanism of the process. Much care should be taken in the kinetic analysis, because the formal approach does not exclude the possibility of wrong interpretation of the kinetic relation-

ships observed. This factor results from the complex nature of thermal dissociation, in which there is no single relationship between the mechanism of the process and its macrokinetic description. However, the kinetic law is a necessary, although insufficient, condition that must be fulfilled by the probable mechanism of the process.

In both earlier and more recent literature on this subject, one can find many formal works on the kinetics of thermal dissociation [9–15]. The authors of these works endeavour to analyse, in a way that is fully correct from both physicochemical and mathematical points of view, the effect of as many factors as possible on the course of the process. They attempt to find the functional form $g(\alpha)$ of the effect of temperature, pressure, changes in particle shape, etc. As a result, there appear kinetic models of very complex construction, which require the use of totally new concepts, for example the so-called inner compensation effect [13,14]. Those models are very far from the true image of the process, and are totally useless for practical description of the kinetics of thermal dissociation of solids.

One can follow here the assumption suggested by Kurt Godl (the author of the fundamental theorem on the imperfectness of arithmetic and the resulting theory of chaos). This assumption appears more and more frequently both in theoretical considerations and in modern scientific laboratories, where an impassable barrier arises and it becomes impossible to preview the further course of a process, in cases where, at an advanced stage of study of a phenomenon, the number of modifying factors becomes too large. Thus it appears that the behaviour of some systems formerly considered as capable of being foreseen and subject to normal casual regularities cannot be described in terms of statistical categories. As an example, we can note that the function of distribution of grain size in a given material, taken into account in the kinetic equation, changes totally the form of that equation and the accepted picture of the process [15]. Such a situation results also, and perhaps first of all, from the absence of a correct and practically useful theory of activation energy and pre-exponential factor in the Arrhenius equation in relation to reactions taking place in a solid [16], despite numerous attempts to elaborate such a theory [17,18].

In practice, analytical data are usually analysed by means of several, at the most 10–20, simple equations, if digital computers are involved in data processing. Most frequently, use is made of about 20 kinetic equations [19]. The kinetic curves obtained experimentally are used for identification of the parameters of the kinetic model (equation) of dissociation of the compound. The identification calculations are usually effected with the use of a previously given flow diagram by means of a digital computer. A criterion for selection of the optimum equation (model) is the value of the standard deviation between the calculated and experimentally found values of $f(\alpha)$ [8].

Another, and seemingly better, procedure is to consider two variants of

description of the results of measurements by means of the least squares method [21]. The variant I, in which $g(\alpha) = kt$ and the variant II, where $g(\alpha) = kt + b$, differ in the value of the constant k connected with non-isothermal conditions of the process. The value of the constant increases with increasing measurement temperature, depending on the transformation degree α attained before the conditions of measurement have been stabilized.

One of the assumptions made in the least squares method is that concerning the stability of the variance of the dependent variable, i.e. $g(\alpha)$. In cases where that assumption cannot be fulfilled, the weighted method of least squares is applied, and the following criteria are applied in making a graph of a function that best correlates with the experimental data

- (i) the correlation factor r ;
- (ii) the correlation factor with regard to the weights;
- (iii) the mean square of the difference (for the given temperature) calculated from the relationship

$$R = \frac{1}{n} \sum_{i=1}^n (\alpha_{ie} - \alpha_{ic})^2$$

where n = number of measured values, α_{ie} = experimentally determined transformation degree for time t , α_{ic} = transformation degree calculated for time t from the function $g(\alpha)$ according to variant I or II;

- (iv) the ratio of S_k/k , i.e. the quotient of the standard deviation and rate constant of the reaction;
- (v) the criterion s described by the relationship

$$s = \frac{1}{N} \sum_{i=1}^l \sum_{j=1}^{n_i} (\alpha_{e,ij} - \alpha_{c,ij})^2$$

where l = number of temperatures, n_i = number of values of α for temperature i , N = sum of n_i values, $\alpha_{e,ij}$ = experimentally determined transformation degree and $\alpha_{c,ij}$ = transformation degree calculated from the Arrhenius equation.

The function of $g(\alpha)$ found by this method and best corresponding to the experimental values should fulfill the following conditions: the values of criteria (i) and (ii) should be close to unity and those of criteria (iii), (iv) and (v) should be minimal with regard to the values of those criteria for the other $g(\alpha)$ functions taken into account.

There is also another method for selection of the $g(\alpha)$ function, which consists in comparing the kinetic curves drawn in the coordinates transformation degree vs. reduced time (the Zawadzki method). The reduced time t_r is the ratio of time t to the time at which a selected value of transformation degree (in most cases 0.5) is attained. If the kinetic curves in the system $\alpha-t_r$ are affinely transformable, they coincide for experiments

carried out at different temperatures. This is indicated by the form of the $g(\alpha)$ function, which describes the decomposition of the given compound throughout the whole temperature range. The choice of that function consists in comparing the experimental curves found by this method with theoretical curves drawn for different forms of the $g(\alpha)$ function.

A modification of the method, seemingly more objective, has been described by Różycki and Maciejewski [22]. The modification consists in the choice of the function $g(\alpha)$ which describes most adequately the experimental data based on calculation of the sum

$$D_i = \sum_{j=1}^m [(t/t_{0.5})_{d,j} - (t/t_{0.5})_{i,j}]^2$$

where $(t/t_{0.5})_{d,j}$ and $(t/t_{0.5})_{i,j}$ are the experimentally found and theoretical values of reduced time for transformation degree j . The value of D_i is calculated for individual temperatures and various functions $g(\alpha)$. The values of D_{sum} are also determined as sums of D_i values for individual temperatures. The minimum of d_{sum} determines the function of $g(\alpha)$ which describes most adequately the experimental data in the temperature region of interest.

The kinetic parameters identified by means of the selected equation, i.e. the Arrhenius activation energy and pre-exponential factor, are very useful for determining the mechanism of the process. The kinetic parameters may also serve for correlation with parameters determined from non-isothermal studies. The correlation is usually made by simulation of thermogravimetric curves (TG and DTG) by means of numerical integration of the equation for reaction rate and the equation that describes the assumed rate of temperature increase with time [20]. Such a simulation is not possible, however, in cases where the course of the thermal dissociation process is identical under both static and dynamic conditions.

If it is not possible to simulate the decomposition of the compound on the basis of kinetic parameters identified in isothermal studies, the method of multiple regression [20] should be used for determining the kinetic parameters under dynamic conditions.

The presented approach to the problem and the methods of description of the process show that the creation and choice of mathematical model for the process require the thorough knowledge of the mechanism of thermal dissociation and of possibilities of its variations under the conditions of the given research problem.

The reliability of kinetic data should also be verified on the basis of general regularities of the thermal dissociation of solids, that is to say, the Zawadzki–Bretsznajder relationship, the compensation effect, the existence of an isokinetic temperature, and the specific correlation between the Arrhenius activation energy and supersaturation. These regularities also have a theoretical justification [23].

The increase, frequently a considerable one, of the Arrhenius activation energy due to increase in the partial pressure of the gaseous reaction products is not always sufficiently compensated by increase of temperature, and if the influence of temperature is described by the Arrhenius equation the value of the pre-exponential factor in this equation must also change in a definite manner. The nature of these changes is described by the compensation equation [24,25], which includes also the isokinetic temperature. The knowledge of the isokinetic temperature enables the determination of experimental values of coefficients in the compensation equation. These coefficients are well correlated with the calculated ones [26], and that correlation is by no means casual, since the values of k , E , T and A are interrelated by the Arrhenius equation and, besides, the values of A and E are in correlation with k and T [23,27,28].

Another regularity found to be experimentally and theoretically justified [16] is the relationship between the activation energy and supersaturation. According to that regularity, the activation energy of a thermal dissociation process calculated from the rate of reaction at various temperatures and constant supersaturation is constant and equal to the Arrhenius activation energy of the process in a vacuum. This correlation has also a practical significance, especially for a process of thermal dissociation carried out close to the state of equilibrium or with accumulation of gaseous reaction product, for which the effect of the reverse reaction can not be excluded. In such a case the determination of kinetic parameters is possible only under conditions of constant supersaturation. The practice shows that the most advantageous is the combination of the two methods of determining the kinetic parameters, and the concordance of the obtained results is not only the criterion of correct choice of the experimental conditions but also permits one to penetrate more deeply in the mechanism of the dissociation.

CONCLUSIONS

Taking account of the procedures presented it can be stated that

- (i) in the study of the stages of thermal decomposition, one should endeavour to approach, as closely as possible, the so-called elementary processes, i.e. the processes limiting the reaction rate in the given stage of dissociation of the compound;
- (ii) the description of the reaction rate should be based on a carefully selected, and simplest possible, kinetic equation, which involves the minimum number of parameters. The situation is the most advantageous in cases where, in isothermal and isobaric measurements, the only variable in the kinetic equation is the reaction rate constant;
- (iii) the results of the studies require careful statistical treatment;
- (iv) the adequacy of the results obtained should be verified with the use and on the basis of the general regularities that control the course of the process.

REFERENCES

- 1 J. Dereń, J. Haber and R. Pampuch, *Chemistry of the Solid State*, PWN, Warsaw, 1975.
- 2 W.W. Bołdyriew, *Influence of Defects in Crystals on the Rate of Thermal Decomposition of Solids*, University of Tomsk, Tomsk, 1964 (in Russian).
- 3 J. Pysiak and B. Pacewska, *J. Therm. Anal.*, 19 (1980) 79.
- 4 B. Lorant, *Fresenius Z. Anal. Chem.*, 219 (1965) 18.
- 5 N. Ueyma, T. Araki and H. Tani, *Inorg. Chem.*, 12 (1973) 2218.
- 6 B. Pacewska and J. Pysiak, *Thermochim. Acta*, 179 (1991) 187.
- 7 J. Pysiak and A. Glinka, *Thermochim. Acta*, 44 (1981) 21.
- 8 J. Pysiak and B. Pacewska, *J. Therm. Anal.*, 19 (1980) 89.
- 9 E.A. Prodan and M.M. Pawluczenko, *Heterogeneous Chemical Reactions, Science and Technics*, Minsk, 1965, p. 20 (in Russian).
- 10 J. Šesták, P. Holba and J. Kratochvíl, *Heterogeneous Chemical Reactions and Reactivity of Solids*, Science and Technics, Minsk, 1975, p. 57 (in Russian).
- 11 J. Šesták, *Measurements of Thermophysical Properties of Solids*, Academia, Prague, 1982 (in Czech).
- 12 J. Šesták, *Theory of Thermal Analysis*, Science, Moscow, 1987 (in Russian).
- 13 A.J. Lesnikowicz and S.W. Lewchik, *J. Therm. Anal.*, 30 (1985) 237.
- 14 A.J. Lesnikowicz and S.W. Lewchik, *J. Therm. Anal.*, 30 (1985) 677.
- 15 J. Pysiak, R. Marcinkowski and B. Podlaska, *Rocz. Chem.*, 47 (1973) 133.
- 16 E.A. Prodan, M.M. Pawluczenko and S.A. Prodan, *Trends in Topochemical Reactions, Science and Technics*, Minsk, 1976 (in Russian).
- 17 W.E. Garner, *Discuss. Faraday Soc.*, 5 (1949) 7.
- 18 N.H. Hartshore, *Discuss. Faraday Soc.*, 5 (1949) 149.
- 19 B. Pacewska, *Studies on thermal dissociation of basic aluminium ammonium sulphate and mathematical model of the process*, Doctoral Thesis, Warsaw University of Technology, 1978 (in Polish).
- 20 J. Pysiak and B. Pacewska, *J. Therm. Anal.*, 19 (1980) 243.
- 21 B. Pacewska, *Thermal decomposition of synthetic compounds of the type of alunite*, Dissertation, Warsaw University of Technology, 1992 (in Polish).
- 22 C. Różycki and M. Maciejewski, *Thermochim. Acta*, 122 (1987) 339.
- 23 J. Pysiak and B. Sabalski, *J. Therm. Anal.*, 17 (1979) 287.
- 24 J. Pysiak and A. Glinka, *Thermochim. Acta*, 44 (1981) 101.
- 25 T. Żmijewski and J. Pysiak, *Therm. Anal., Proc. Int. Conf.*, 4th, Budapest, 1974, Vol. 1, p. 205.
- 26 J. Pysiak, *Methods of study of thermal dissociation of solids*, Paper presented at the 3rd St. Bretsznajder Seminar, Płock, Poland, 1983.
- 27 J. Pysiak, *Regularities in the thermal dissociation of solids*. *Thermal Analysis*, Bor, Yugoslavia, 1984.
- 28 J. Pysiak, *Regularities in the kinetics of thermal dissociation of solids*, Paper presented at the 2nd St. Bretsznajder Seminar, Płock, Poland, 1979.