SOMEWHERE BETWEEN FICTION AND REALITY
The usefulness of kinetic data of solid-state reactions

M. Maciejewski

DEPARTMENT OF INDUSTRIAL AND ENGINEERING CHEMISTRY, SWISS TECHNICAL INSTITUTE OF TECHNOLOGY, CH-8092 ZÜRICH, SWITZERLAND[*]

The influence of various experimental conditions such as sample weight, atmosphere and heating rate on the decomposition of NH_4VO_3, $CaCO_3$ and V_2O_5 has been investigated. Results obtained clearly indicate that the course of the reactions and - in turn - the kinetic parameters, are not intrinsic to the particular compound and that they characterize rather the combination of experimental conditions and investigated compound. Such a situation makes it almost impossible to choose 'standard conditions' for the calculation of kinetic parameters, because under different circumstances quite different reaction-pathways can occur.

Keywords: kinetics, solid-state reactions

Introduction

The interpretation of the kinetic parameters of the solid-state reactions (i. e. the activation energy E, pre-exponential factor A, the form of the function $g(\alpha)$ dependent on the course of the reaction and so called 'reaction order' n) has for many years provoked vigorous discussion. These parameters, taken from the kinetics applied in homogeneous systems, are used for the description of the reactions occurring in the solid state, where their physico-chemical meaning is rather open to debate – this problem has been discussed at many Congresses (i.e. round table discussion on VIII-th ICTA, Bratislava 1985, IVth ESTAC, Jena 1987 or Ist Int. Symp. 'Reactivity of Solids', Novosibirsk 1988) and in many papers. It is obvious, that the quantitative description of the solid-state reactions is necessary and useful in many

---

[*] On leave from Warsaw University of Technology, Warsaw, Poland.

theoretical and industrial applications – but one can accept without difficulties only such a treatment of above mentioned parameters, when they are used as mathematical expressions only. In very rare cases their interpretations can lead to useful information concerning the course of the reaction (commonly known as a 'mechanism').

The large majority of calculation methods of E, A or g (α) and later their interpretations are based on the assumption that these parameters are intrinsic, therefore characteristic for the decomposed solid. This statement leads to misunderstandings, because for solid-state reactions even answer to the very simple question: '...what is the product of the decomposition of the compound X ...' could be incorrect – depending on the experimental conditions quite different products or intermediates could exist in the investigated system. Of course, the influence of the experimental circumstances on the course of the solid reactions can be very different – from very strong, as for reversible, endothermal decomposition reactions, to negligible, as for pure solid-state reactions (i.e. polymorphic transitions or crystallization of the amorphous solids). Even knowing how conditions of the experiment are influencing the course of the reaction and their kinetics – one can not treat the obtained data as an intrinsic parameters. Presented in this paper such reactions as reduction of V_2O_5 by hydrogen or decomposition of $CaCO_3$ cannot each be described by one, universal set of kinetic parameters, and data determined from particular experiment are – generally – characteristic not for the investigated compound, but for the system: investigated compound-experimental conditions-method(s) of calculation. This obvious statement is as often widely accepted, as forgotten.

The aim of this paper was to present some factors influencing the course of the solid-state reactions. Some of them are important in some cases only, but being satisfied that method used gives the possibility of the determination of the kinetic data '... from one experiment only ...', it is necessary to keep in mind, how easy it is to cross the barrier between reality and fiction, during interpretation of the kinetic data of the solid-state reactions.

For the illustration of the above remarks, the influence of the various experimental conditions on the course of different types of solid-state reactions has been chosen:
- reversible decomposition of $CaCO_3$
- reversible reduction of V_2O_5 by hydrogen
- irreversible decomposition of ammonium metavanadate NH_4VO_3

The following parameters have been investigated:
A – the change of the mass of the reactant

B – the change of the atmosphere in the system, particularly:
- influence of the partial pressure of the gaseous product
- influence of the inert gas flow
- influence of the kind of the inert atmosphere

C – heating rate and concentration of reactive gas in the case of the reaction between gas and solid.

D – chemical interaction of the gaseous product with the solid intermediates or products.

A. The influence of the mass of the reactant on the calculated kinetic parameters

This problem has been examined and reported in a few papers [1–8] and generally it has been found that for reversible decomposition process, the
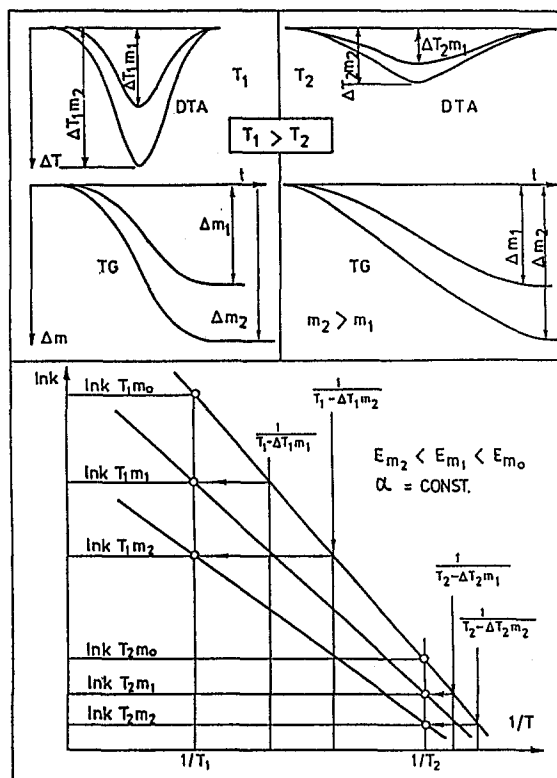

Fig. 1 The influence of the sample mass on the course of the relationship $\ln k-1/T$. $\Delta T_1 m_1$ and $\Delta T_2 m_2$ – the decrease of the temperature of the sample at $\alpha = 0.5$ for the samples with masses m_1 and m_2 ($m_2 > m_1$) at the temperatures T_1 and T_2, respectively ($T_1 > T_2$). The ΔT for $m_0 = 0$ is equal 0

change of the mass influences the course of the reaction. There are two obvious reasons explaining this observation:

– the increase of the mass increases the concentration of the gaseous product in the surrounding atmosphere, which – in turn – generally shifts the range of the reaction up to higher temperatures.

– the increase of the mass leads to a larger change of the temperature profile inside the sample due to the self-cooling (or self-heating) process, caused by the heat of the reaction.

This last phenomenon has been reported in a few publications (see e. g. [9–11]), where the non-isothermicity during decomposition has been determined. The smaller the rate of the reaction is (i.e. the lower the temperature), the more negligible this self-cooling effect is, and only at higher reaction rates does the effect become visible. Such a relationship has to influence the calculated activation energy – the explanation of this statement is presented in Fig. 1 for the iso-conversional method of calculating E (in the present case for $\alpha = 0.5$). The larger the sample size of the reactant is, the lower the activations energy – of course this relationship depends strongly on the mass of the reactant and its physical properties. In case of small masses (10–20 mg) and moderate value of the heat of the reaction (20–30 kcal/mol), the temperature
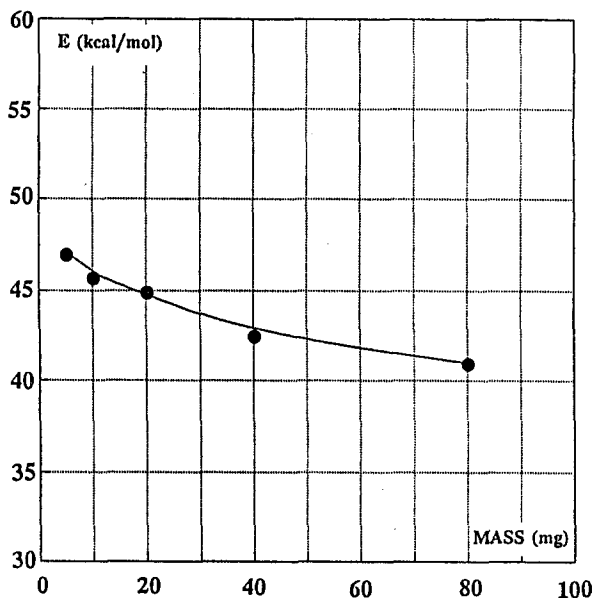

Fig. 2 The relationship between the sample mass and the activation energy of CaCO3 decomposition

difference at the maximum of the reaction rate has order of magnitude of 2−4 degrees, but even this is enough, to change the calculated E values. Experimental data confirming above remarks are presented in Fig. 2. Obtained results − being generally consistent with those reported in the literature − clearly indicate one of the source of the discrepancies made in the interpretation of the physical meaning of the kinetic parameters.

B. The influence of the atmosphere

The influence of the partial pressure of the gaseous product on the reversible decomposition of solids is obvious and observed in many cases. Recently this problem has been described by Garn [12], see also papers [13−17]. There is a lack of experimental quantitative data concerning this problem among hundreds of papers dealing with kinetic experiments. One reason is caused by the fact, that the generally used equation in solid-state kinetics i.e. $g(\alpha) = kt$ does not include the pressure dependent term. This problem has been already discussed in [18−20].

The influence of the gaseous product pressure can be different:
− in the simplest case its increase will shift only the reaction range to higher temperatures.
− under higher partial pressure of the gaseous product, the change of the course of the reaction can not be excluded in some specific cases, as i.e. when a few intermediates can be produced in the reaction − see data for $PbCO_3$ or $CuSO_4 \cdot 5H_2O$ decomposition [21−28].
− when the reaction is being shifted to higher temperatures due to higher partial pressure of the product gas, additional phenomena can occur. In case of $CaCO_3$ decomposition, sintering of the product prior to decomposition under pressures of CO_2 in the range 50−1000 mb has been reported [27−30]. Also, the change of shape of the TA-curves when the concentration of the product gas is changed can suggest the change of the kinetic parameters (see below).

B1. The influence of the concentration of the gaseous product

The decomposition of the $CaCO_3$ (calcite, p.a., Merck) under different pressure of CO_2 has been investigated under non-isothermal conditions. The results presented in Fig. 3 show two phenomena: the shift of the temperature range and distinct change of the shape of the TA-curves. The first observation is clear from the thermodynamic point of viewreaction starts at such a

temperature, when the equilibrium partial pressure of CO_2 in the system $CaCO_3$–CaO–CO_2 is higher than partial pressure of CO_2 in the investigated system. The second observation is rather unexpected- such a variation of the shape of DTA or DTG curves indicates their lack of affinity, which according to the generally applied meaning is characteristic for a case, when the change
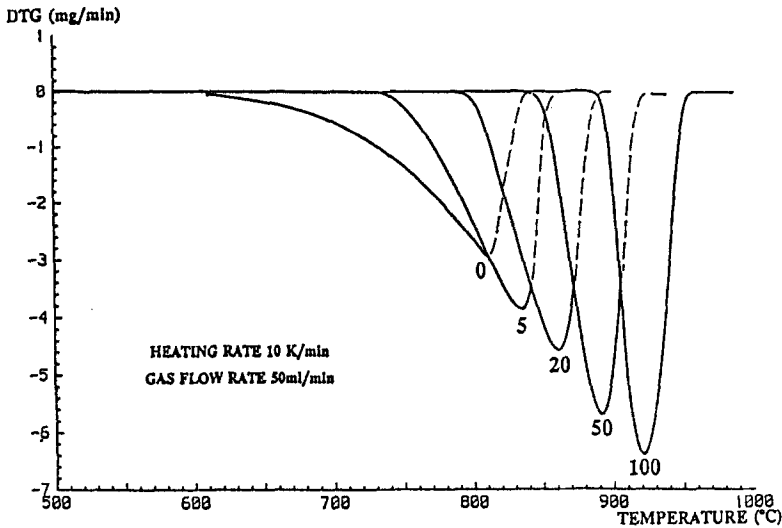

Fig. 3 The rate of $CaCO_3$ decomposition (DTG curves) as a function of CO_2 concentration (vol-% in the mixture Ar-CO_2)
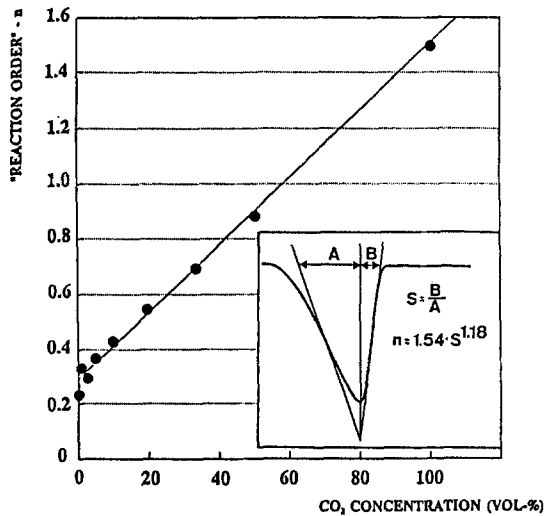

Fig. 4 Thermal decomposition of $CaCO_3$ – the relationship between CO_2 concentration and the 'reaction order' n calculated according to Balarin [33]

of the reaction mechanism takes place. On the basis of this change of shape of the DTA (DTG) curve a few methods for the determination of the 'reaction order' n have already been proposed [31−33]. Results of such calculations based on the Balarin method [33] are presented in Fig. 4. It is not the aim of this paper to discuss whether the parameter n calculated in such a way has any physical meaning – the purpose of the presentation of the above results is to show that pressure of the gaseous product of the reaction could be an important factor changing the mathematical description of the process. Results presented in Figs 3 and 4 show that is rather impossible to describe the decomposition of $CaCO_3$ under different pressures of CO_2 using the same $g(\alpha)$ function. Any change in the experimental conditions influencing the CO_2 concentration will lead to the change of the factor n which – in turn – makes rather useless its application as a factor characteristic for the investigated solid.

B2. The influence of the rate of the inert gas flow

For the reactions sensitive on the gaseous product concentration, the flow-rate of the inert purging gas can influence their course. This problem has been reported in [1, 34, 35, 6]. In this last work the change of the flow of the nitrogen from 20 to 35 cm^3 caused – in the opinion of the authors – a 'change of the mechanism of decomposition from R2 to R3'.

The influence of the change of the inert gas flow on the decomposition reaction depends mainly on such experimental factors as the sample size, geometrical localization of the gas in- and outlet $vs.$ sample holder, the kind of crucible used, the conditions of mixing of both gaseous streams and the kind of purging gas. This problem is of great importance when a thermoanalyser is coupled to the mass spectrometer (MS), and the proper value of the gas flow is one of the main factors affecting the mutual relationship between TA and MS data.

The calculated relationship between the concentration of the gaseous product and the flow rate of the inert gas taken from [36] is presented in Figs 5 and 6 are submitted the experimental data concerning the change of the CO_2 concentration during $CaCO_3$ decomposition. The influence of the flow rate of argon on $CaCO_3$ decomposition is presented in Fig. 7 – increase of the argon flow – decreasing the CO_2 concentration – shifts the temperature range of the decomposition into lower temperatures. Such a shift has influence on the kinetic parameters, being the numbers or functions, describing the position of the curve, representing the course of the decomposition, in the coordinates alpha $vs.$ time or temperature.
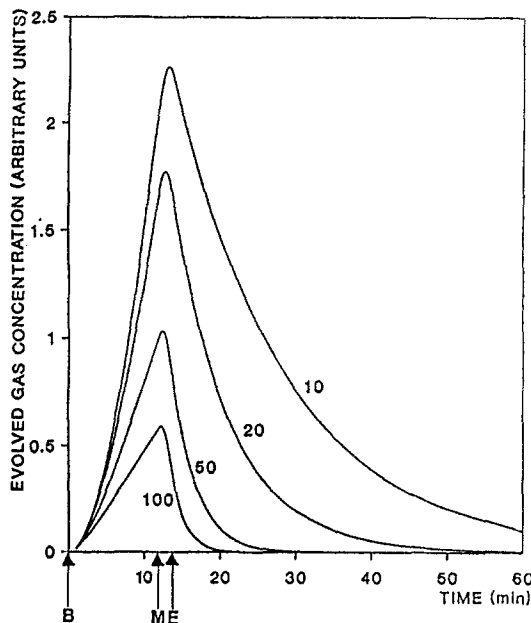
Fig. 5 The calculated relationship between concentration of the evolved gas, flow-rate of the purge gas (marked in ml/min on the curves) and time for the following parameters: the volume of the reaction space 150 ml, the maximal rate of the gaseous product evolution – 0.672 ml/min. The arrows indicate the beginning (B), maximum (M) and the end (E) of the decomposition
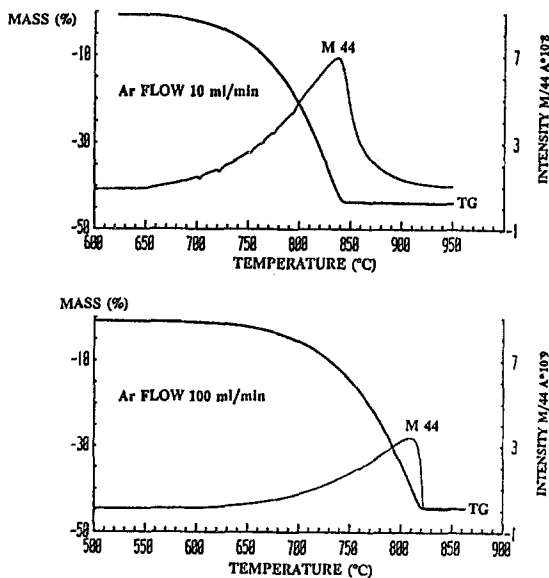

Fig. 6 The influence of the inert gas-flow on the course of TA and MS curves for $CaCO_3$ decomposition. Note the difference of the sensitivity of the scale of the mass 44
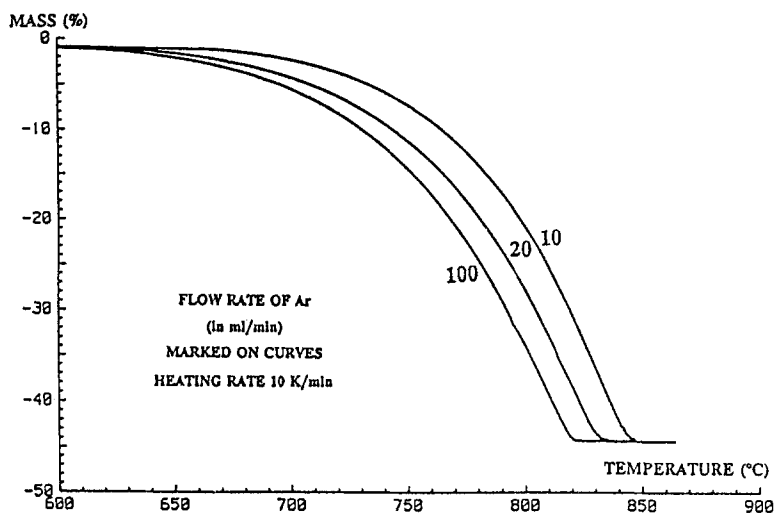
Fig. 7 The influence of the inert gas-flow on the course of TG-curves of CaCO₃ decomposition.

B3. The influence of the kind of the inert atmosphere

This problem has been reported in a few papers, see e.g. [1, 34]. It is obvious that physical properties of the purge gas such as thermal conductivity, specific heat, diffusion coefficients of product – and inert gases, influence the course of the decomposition. All these factors can play some role especially when sample mass is large, but would be rather unexpected to predict, that the change of the conditions of the heat – and mass exchange (i.e. the change of the kind of the atmosphere) could lead to the visible altering of the reaction course in the case of small samples (10–20 mg), when thermal effects during decomposition are not large. The experimental results do not confirm these expectations – data presented in Fig. 8 concerning the $CaCO_3$ decomposition under He, N_2, Ar and Kr show distinct influence of the kind of the inert atmosphere on the reaction course. These results are coincident with those one reported by Criado [34] and Reich [6], who found also, that if molecular weight of the purge gas is increased, the DTA or DTG peaks are shifted up to higher temperatures. Such a phenomenon took place only for reversible decomposition reactions – for irreversible reactions in the system gas-solid [34] or for reversible transformations occurring in the solid state only (polymorphic transformation of KNO_3, K_2SO_4, $KClO_4$ and K_2CrO_4 [37]) the change of the course of the reaction is very small (or even negligible) despite the different physical properties of the purge gas. These observations lead to the conclusion that the kind of the atmosphere (particularly its

molecular weight) influences the course of the reaction, lowering or ac-
celerating the rate of the back reaction – in this case synthesis of $CaCO_3$ from
CaO and CO_2. Discussion of this problem will be published in separate paper
[36], but even on the basis of the above presented data, one can clearly see
that, under different atmospheres, different sets of the kinetic parameters are
needed for describing the reaction. The shift of the DTG peak during $CaCO_3$
decomposition of about 50 degrees, when atmosphere is changed from He to
Kr, will obviously lead to the change of the kinetic parameters. It is also ob-
vious that for experiments carried out under vacuum, where gaseous product
is continuously removed from the system, the back reaction in a reversible
process will be inhibited, and that – in turn – will lead to large differences in
the course of the reaction, changing e.g. the morphology of the product [29,
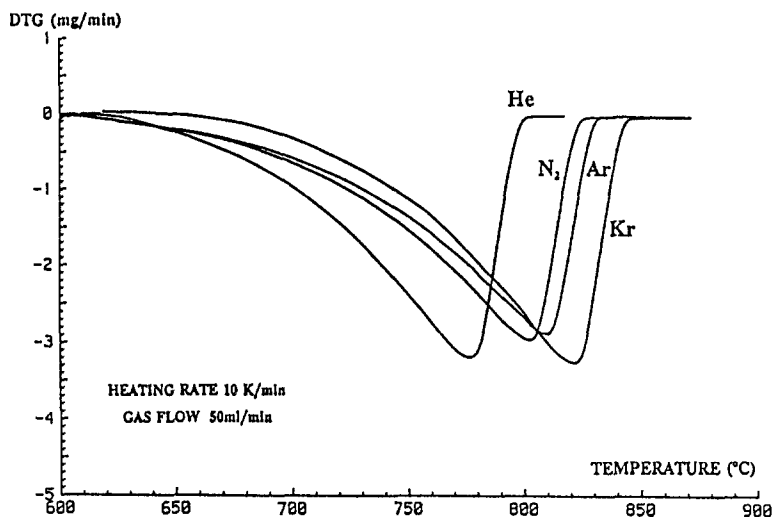30, 38−40] and kinetic behaviour.

Fig. 8 The rate of $CaCO_3$ decomposition under different atmospheres

Above remarks are illustrated by the data presented in Fig. 9, showing the
sets of the experiments made with $CaCO_3$ at constant temperatures under dif-
ferent atmospheres (N_2, CO_2 and vacuum). One can observe the quite dif-
ferent shape of TG-curves, indicating the different form of the $g(\alpha)$ function
describing the α-time relationship, and distinct differences of the tempera-
ture range of the reaction (temperatures in above isothermal runs have been
chosen such a way, that the time interval of the reaction has been similar for
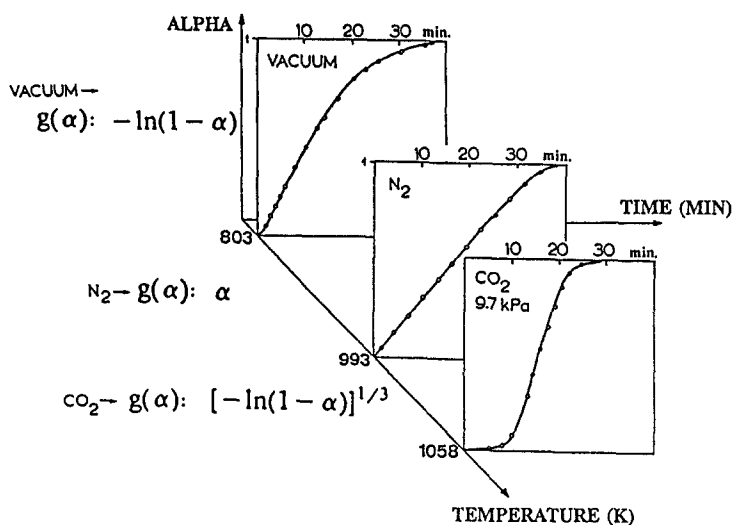all experiments).

Fig. 9 The relationship $\alpha - t - T$ for the isothermal decomposition of $CaCO_3$ under vacuum, nitrogen and CO_2. The functions $g(\alpha)$ the best describing the course of the reaction are marked on the figure

Presented data show the common source of the misunderstandings expressed e.g. by the sentence '... the true kinetic data have been obtained under the following conditions ...'. The change of the experimental conditions can lead to the enormous change of all the kinetic parameters, but all of them – if of course properly calculated – are true for particular system: the investigated compound – the circumstances used. The belief that one can extrapolate obtained data to some 'standard conditions' let us say to $p = 0$, could be very often not proper enough. Under the different conditions, quite another course of the reaction could occur, because quite different basic steps of the process as e.g. nucleation, chemisorption or diffusion could become the phenomena controlling the total reaction rate.

C. The influence of the heating rate and concentration of the reactant gas in case of the reaction between gas and solid

The results and comments presented above considered the course of the reversible decomposition reactions being the simplest case – when one product only has been in every case the final step of the process and no intermediates have been created during the course of the reaction. The calculation and use of the kinetic parameters and the interpretation of their physical

meaning is much more difficult, when during solid-state reaction a few inter-
mediates can occur. As an example of such a reaction the reduction of V_2O_5
by hydrogen has been chosen.

Considerable effort has been expended to investigate the different inter-
mediate oxides existing in the composition range V_2O_5 – V_2O_3, see e.g.
[39–48]. Stringer [41] suggests the existence of 12 oxide phases in this com-
position range, also 12 phases of vanadium oxides with the composition be-
tween V_2O_5 – V_2O_3 are reported in the set of X-ray diffraction patterns edited
by JCPDS [49]. A lot of the existing uncertainties about the existence and the
stoichiometry of the intermediates are caused – among others – by the strong
influence of the experimental conditions on the course of the reaction. In
such a situation, the attempts of the interpretations of the kinetic data have to
be made very carefully. Presented below experimental results show, that is al-
most impossible to try to describe the reaction of V_2O_5 reduction by one,
characteristic for this reaction, set of kinetic parameters, they indicate also
the questionability of the physical meaning of the very simplified forms of the

TG CURVE DESCRIBED BY THE
KINETIC PARAMETERS
$g(\alpha) = [1-(1-\alpha)^{1/3}]^2$
$E = 42000$ cal/mol
$A = 1.300$ c^{-1}
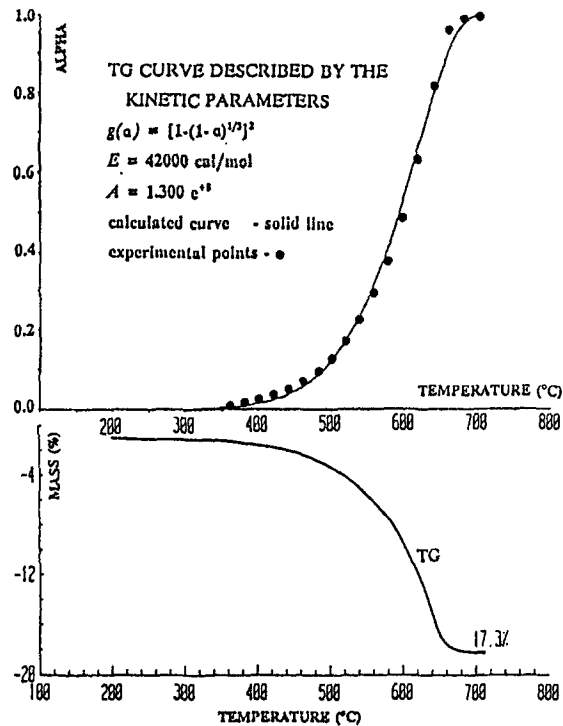calculated curve - solid line
experimental points - •

Fig. 10 TG-curve of the reduction of V_2O_5 by hydrogen (lower part). The same experimental
data described by the kinetic parameters (upper part)

$g(\alpha)$ functions, theoretically based on the 'real mechanism of the solid-state reactions'.

In the lower part of Fig. 10, the TG curve of the reduction by hydrogen of the V_2O_5 sample produced by the decomposition of ammonium meta-vanadate (AMV) under vacuum is presented. The reduction has been carried out with the heating rate 2.5 deg/min and concentration of H_2 in the Ar of 6%. In the upper part of Fig. 10, the fit of kinetic calculations by the experimental results is included – the function, the best describing the full course of the process is representing by the equation proposed by Jander [50]:
$g(\alpha) = [1-(1-\alpha)^{1/3}]^2$. The knowledge of this function, describing well the reaction from mathematical point of view, does not increase the information about the real course of the process. How complicated is this reaction is shown in Fig. 11, where the X-ray diffraction data obtained in high-temperature camera (Siemens Diffractometer 5000 equipped in HTK 10, Pahr, Austria) are presented.
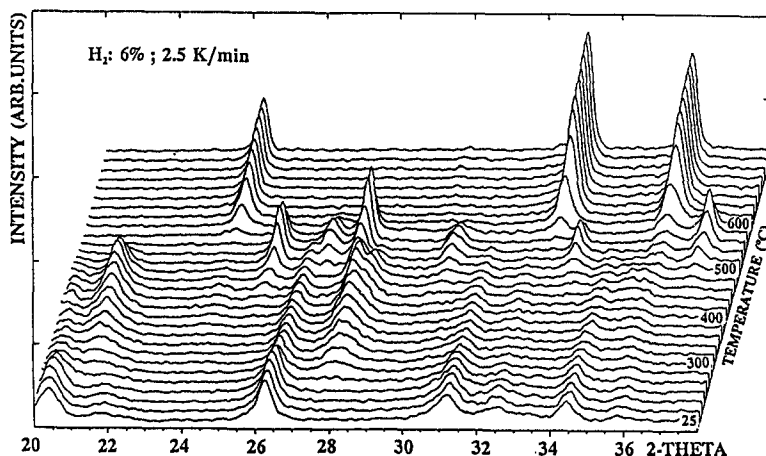

Fig. 11 High-temperature X-ray analysis of the reaction of V_2O_5 reduction by hydrogen. Presented data show the following sequence of the existence of the vanadium oxides: $V_2O_5 - V_4O_9 - VO_2 - V_2O_3$.

Systematic investigations concerning the course of the V_2O_5 reduction as a function of H_2 concentration, heating rate and the kind of reactant (commercial product p.a. from Fluka-Switzerland, product of AMV decomposition under vacuum and amorphous vanadia obtained by sol-gel technique) [51] show tremendous differences between experiments. The influence of the hydrogen concentration is presented in Fig. 12, the influence of the heating rate – in Fig. 13. All these relationships are also varying according to the kind

of vanadia; even different intermediates are produced as a first stable phase (V_6O_{13}, V_4O_9 or V_3O_7) depending of the origin of the reactant.

In such a complicated system it is rather impossible to predict the course of the reaction under slightly – only – changed conditions. One can find on TA-curves one peak (vanadia gel, H_2 concentration –25%, heating rate 10
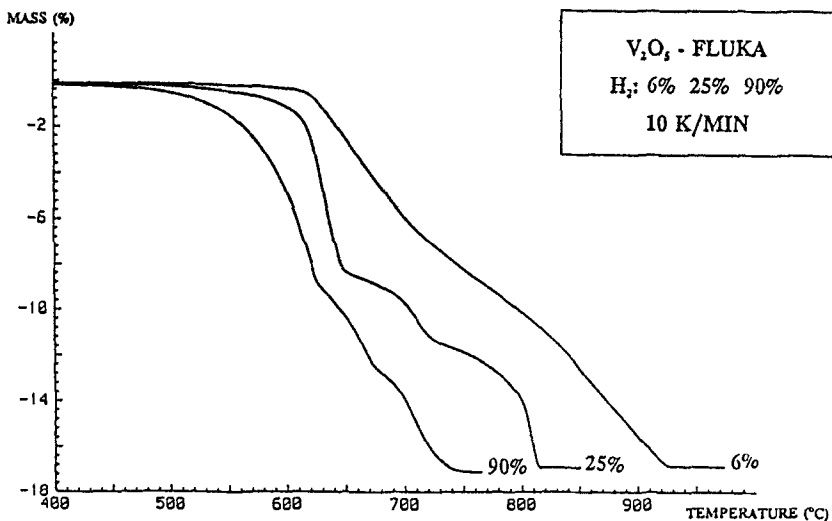
Fig. 12 The influence of the concentration of H_2 (marked on curves) on the course of TG-curves of V_2O_5 (Fluka, p. a.) reduction
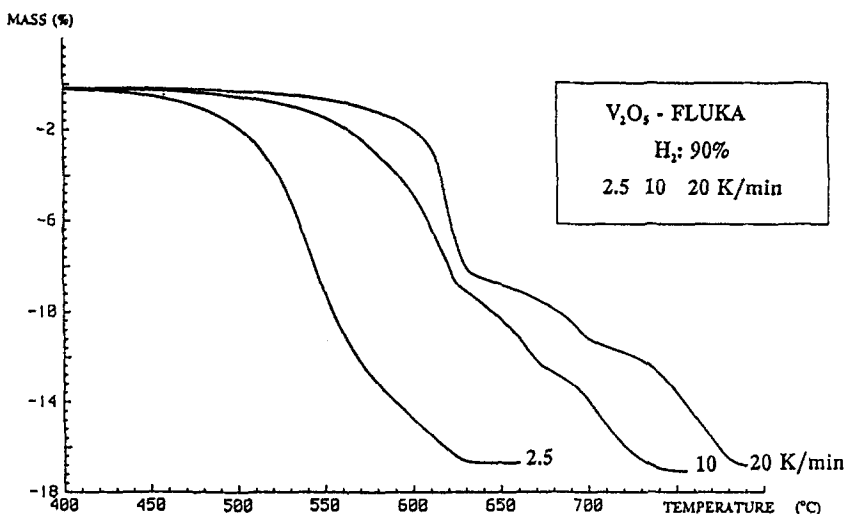
Fig. 13 The influence of the heating rate (marked on curves) on the course of TG-curves of V_2O_5 (Fluka, p. a.) reduction

deg/min), two (V_2O_5 from AMV, H_2- 90%, Φ-2.5 deg/min) or even three (V_2O_5-Fluka, H_2- 25%, Φ-10 deg/min). The difference between the temperature ranges of V_2O_5 reduction for particular samples and particular experimental conditions, can reach the value of more than 400 K (the lowest temperature of the end of the reaction under low heating rate and high H_2 concentration was 470°C, the highest- 885°C, see data in Fig. 14).
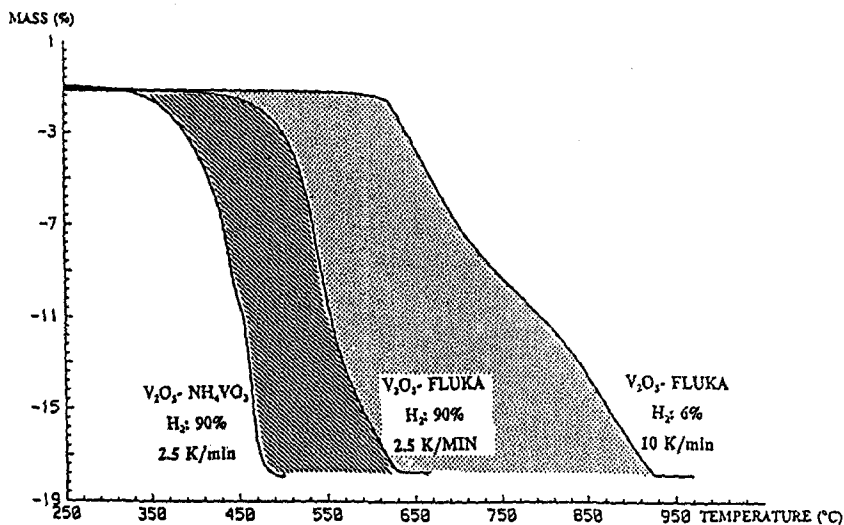

Fig. 14 The temperature range of the V_2O_5 reduction as a function of the heating rate and concentration of H_2. The area presenting the data for the same sample (V_2O_5-Fluka) is dotted, the additional area for the another sample is hatched

One of many reasons leading to such great differences in the course of the vanadia reduction is the occurrence of additional phenomena in the system, when the heating rate is increased. From a kinetical point of view, the increase of Φ shifts the reaction to higher temperatures – the calculated curves for the Φ in the range 1.2−20 deg/min and for constant values of E, A and $g(\alpha)$ are presented in Fig. 15 – kinetic parameters have been chosen so as to give the same relationship α-T, as has been obtained experimentally under some conditions. Presented curves show that in case of low heating rates (1.2 and 2.5 deg/min) at the temperature 960 K, the progress of the reaction is in the range 0.25−0.35, but for higher Φ is below 0.1. In this second case, at 960 K will occur the melting of the still unreduced V_2O_5, which – in turn – will change distinctly the course of the further reactions. On the DTA curves one can observe additional endothermal peaks (the reductions of V_2O_5 and all intermediates by H_2 are exothermal) caused by the existence of the liquid

phases in the system, such as melting of vanadia or congruent melting of one
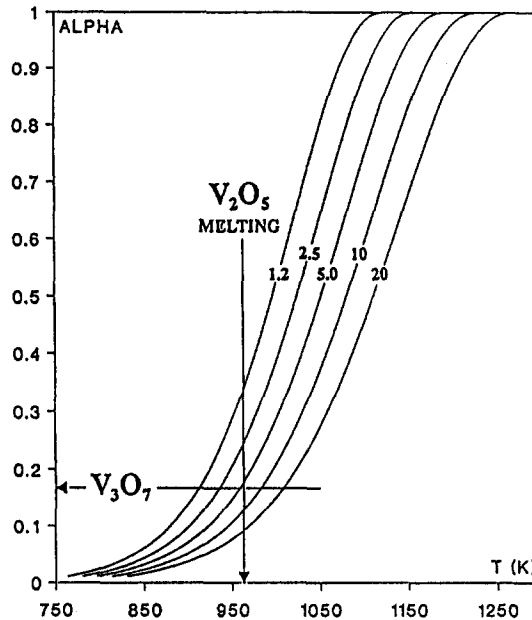of the intermediates, V_6O_{13} (compare data in [47]).

Fig. 15 The influence of the heating rate (marked on curves) on the relationship $\alpha - T$ for
the following kinetic parameters: $E = 50000$ cal/mol, $A = 1.3 \cdot 10^8$, $g(\alpha) = [1-(1-\alpha)^{1/3}]^2$.
On the axis of T and α are shown: the temperature of the melting of V_2O_5 and the
progress of the reaction when V_3O_7 is produced, respectively

Presented above results indicate, how dangerous could be sometimes the
interpretation of the kinetic data obtained under different heating rates or
different concentrations of the reactive gas. Due to the occurrence of the
varying amounts of the intermediates or additional physical phenomena, one
can conclude from the results concerning quite different pathways of the
reaction. In such a situation the following expressions (real citation from one
of the recent literature data): '... the reduction of V_2O_5 was found to be
described by the first-order kinetic equation, and activation energy of 33.2
$kJ \cdot mol^{-1}$ was calculated...' could be true only for the experimental conditions
used, but can not describe the general kinetic behavior of V_2O_5 reduction, be-
cause such a general behavior does not exist.

D. The influence of the chemical interaction of the gaseous product with the solid intermediates or products

In the both described above reactions (decomposition of $CaCO_3$ and reduction of V_2O_5) the final products – depending on the experimental conditions – were always the same, i.e. CaO and V_2O_3, respectively. A more complicated situation can occur, when the final product or one of intermediates can react irreversibly with the gaseous product. Such a situation could be illustrated by the thermal decomposition of ammonium meta- vanadate.

There are a lot of discrepancies concerning the final product of this reaction, caused by the possibility of the reduction of the intermediate product(s) by the evolved ammonia [52–55]. Under air the loss of the weight is 22.9%, theoretical weight-loss in case of V_2O_5 production is 22.2%. Under He or N_2 experimental weight-loss was 25.0% (theoretically when V_3O_7, V_4O_9 or V_6O_{13} are produced, the changes of the weight would be 24.5, 25.6 and 26.8%, respectively). XRD-data confirmed that under air only one phase-V_2O_5 is detectable. In case of the decomposition under He or N_2, the product is the mixture of V_3O_7 with small part of V_6O_{13}.

Experiments carried out in high-temperature XRD camera and thermoanalyser coupled with mass spectrometer confirmed, that the first two stages of AMV decomposition under air or inert gas are similar. The main part of ammonia and water is evolved in the first stage, after second stage in both cases a badly crystalline, almost amorphous intermediate is produced. This phase is reduced by the rest of the NH_3, evolved above 640 K to mixture of oxides V_3O_7 and V_6O_{13}, whereas under air the NH_3 is oxidized by the oxygen taken from the gaseous phase.

Above results are consistent with the results of the experiments carried out under vacuum. In this case, when NH_3 was continuously removed from the system, the final phase was detected by TA and XRD-data as the V_2O_5.

It is clear that in the situation, when the kind of the final product of the reaction depends on the atmosphere of the reaction, it is even impossible to write stoichiometric equation characterizing the general decomposition behavior of NH_4VO_3. All kinetic parameters of this reaction will depend on the respective processes occurred under particular conditions and could never be treated as an intrinsic parameter of this compound.

Conclusions

The quantitative description of the rate of solid-state reactions, based on the use the Arrhenius equation, leads to the parameters which have some physical meaning in homogenous systems. On the other hand, the exponential form of this equation, generally fits the majority of the experimental data obtained for solid-state very well, which in turn leads to the very common opinion that such a parameters as E, A or $g(\alpha)$ also have, in condensed systems, the similar meaning to the case of ideal gases, or even more, that they can help in the understanding of the so called 'mechanism' of solid-state reactions. According to the common way of the interpretation of E, A or $g(\alpha)$, these parameters are characteristic for the investigated compound and can help in the understanding and interpretation of its thermal behavior. The observed differences in the course of the thermal decomposition of a particular solid, caused by the influence of experimental conditions, tend to be omitted by the extrapolation of the obtained results to some 'standard conditions' or by using 'standard methods', giving in the opinion of the users 'real' or 'true' values of the kinetic parameters.

The experimental data presented in this paper show the possible incorrectness of such a procedure. The influence of a large number of variables on the course of the solid-state reactions indicate that their course is not an intrinsic parameter for the investigated compound. All of the data obtained under various circumstances are true (if correctly calculated!) for the applied experimental system only, and the extrapolation of the course of the reaction to different conditions could be incorrect. In the another experimental system, different intermediates (see presented data for V_2O_5 reduction) or even different final products (see data for NH_4VO_3 decomposition) could be formed. The change in mass – due to the unavoidable thermal effect and change of the amount of the gaseous product – influ-ences the relationship in the system $\ln k - 1/T$. The change of the partial pressure of the gaseous product changes the mathematical parameters describing the process (see $CaCO_3$ decomposition), and the process can also be influenced by: the heating rate (in case of the possible occurrence of the additional phenomena caused by the shifting of the reaction range up to higher temperatures – see V_2O_5 reduction), the concentration of the reactive gases, the type and flowrate of the inert purge gas etc.

One can find the reactions less sensitive to the experimental conditions. when the course of the reaction and – in such a case – also the kinetic data are almost independent of the circumstances – but this is an exception to the general behavior of solid systems. In such a situation the following procedure

seems to be acceptable: given that, for whatever reason, the quantitative characterization of the process is required, it is necessary to treat the kinetic parameters as mathematical numbers only, which describe the course of the reaction under particular conditions. but which do not have particular physical significance and are not intrinsic to the investigated compound.

The discussion of the possible misinterpretations where kinetic parameters are applied for mathematical description of the solid-state reactions, will be published in the second part of this paper.

References

1 P. K. Gallagher and D. W. Johnson, Thermochim. Acta, 6 (1973) 67.
2 P. Murray and J. White, Trans. Brit. Ceram. Soc., 54 (1955) 189.
3 J. M. Criado, F. Rouquerol and J. Rouquerol, Thermochim. Acta, 38 (1980) 109.
4 K. N. Ninan and C. G. Nair, Thermochim. Acta, 74 (1984) 143.
5 K. N. Ninan and C. G. Nair, Thermochim. Acta, 37 (1980) 161.
6 C. Bayane and N. Gerard, Thermochim. Acta, 103 (1986) 51.
7 L. Reich, S. H. Patel and S. S. Stivala, Thermochim. Acta, 138 (1989) 147.
8 R. Salvador, E. Garcia Calvo and C. Beneitez Aparicio, Thermochim. Acta, 143 (1989) 339.
9 M. T. Anous, R. S. Bradley and J. Colvin, J. Chem. Soc., 1951, 3348.
10 G. Várhegyi, Thermochim. Acta, 57 (1982) 13.
11 S. S. Alves, Thermochim. Acta, 157 (1990) 249.
12 P. D. Garn, Thermochim. Acta, 160 (1990) 135.
13 J. Zawadzki and S. Bretsznajder, Trans. Farad. Soc., 34 (1938) 950.
14 M. M. Pavljucenko and E. A. Prodan, Vth Int. Symp. of React. Solids, Ed. G. Schwab, Elsevier, Muenchen, 1964.
15 J. Rouquerol, J. Thermal. Anal., 5 (1973) 203.
16 P. Barret, Compt. Rend., 266C (1968) 856.
17 G. Bertrand, J. Thermal. Anal., 13 (1978) 525.
18 N. Z. Lyakhov, M. Maciejewski and A. Reller, J. Solid State Chem., 58 (1985) 398.
19 N. Z. Lyakhov, Izv. Sib. Otd. AN SSSR, ser. Chim. Nauk, 2 (1985) 9. (in Russian)
20 M. Maciejewski and J. Baldyga, Thermochim. Acta, 92 (1985) 105.
21 M. Maciejewski, Bull. Acad. Pol. Sci., Ser. Chim., 18 (1970) 711.
22 M. Maciejewski and J. Leyko, Bull. Acad. Pol. Sci., Ser. Chim., 18 (1970) 81.
23 Z. C. Zivkovic, J. Thermal. Anal., 16 (1979) 3.
24 S. Sarig and F. Kahana, Thermochim. Acta, 14 (1976) 263.
25 M. C. Ball and M. J. Casson, J. Inorg. Nucl. Chem., 37 (1975) 2253.
26 N. Z. Lyakhov, A. P. Chupakhin, V. P. Isupov and V. V. Boldyrev, Kinet. Katal., 19 (1977) 84. (in Russian)
27 S. El-Houte, M. El-Sayed Ali and O. Toft Sørensen, Thermochim. Acta, 138 (1989) 107.
28 M. Maciejewski and H. R. Oswald, Proc. IIIrd Int. Conf. to Mem. S. Bretsznajder, Plock, 1983. (in Polish)
29 M. Maciejewski and H. R. Oswald, Thermochim. Acta, 85 (1985) 39.
30 H. E. Kissinger, Anal. Chem., 29 (1957) 1702.
31 H. Anderson, E. Witte and D. Haberland, J. Thermal. Anal., 21 (1981) 327.
32 M. Balarin, Thermochim. Acta, 33 (1979) 341.
33 J. M. Criado and J. M. Trillo, J. Thermal. Anal., 9 (1976) 3.
34 G. M. Swallowe, Thermochim. Acta, 65 (1983) 151.
35 M. Maciejewski and J. Baldyga, in preparation.

36 M. Maciejewski, unpublished data.
37 M. Maciejewski, Thermal Decomposition of Solids – Determination, Reliability and Usefulness of the Kinetic Parameters, Ed. Warsaw Univ. of Technol. Publ., Warsaw 1988 in Polish.
38 D. Beruto and A. Searcy, J. Chem. Soc., Farad. Trans., 70 (1970) 2145.
39 D. Beruto and A. Searcy, Nature, 263 (1976) 221.
40 J. Stringer, J. Less-Common Met., 8 (1968) 1.
41 G. Anderson, Acta Chem. Scand., 10 (1956) 623.
42 F. Theobald, R. Cabala and J. Bernard, J. Solid State Chem., 17 (1976) 431.
43 K. Kosugo, J. Phys. Chem. Solids, 28 (1967) 1613.
44 T. Sata, E. Komada and Y. Ito, Kogyo Kagaku Zasshi, 71 (1968) 643.
45 H. Bosch, B. J. Kip, J. G. van Ommen and P. J. Gellings, J. Chem. Soc., Farad. Trans. I, 80 (1984) 2479.
46 M. Maciejewski, A. Reller and A. Baiker, Thermochim. Acta, 96 (1985) 81.
47 F. Stander and C. P. van Vuuren, Thermochim. Acta, 165 (1990) 73, 85.
48 Powder Diffraction File, set 1-39, Ed. JCPDS International Centre for Diffraction Data, Pennsylvania, USA.
49 W. Jander, Z. Anorg. Allg. Chem., 163 (1927) 1.
50 M. Maciejewski and A. Baiker, will be published.
51 V. Šatava, Coll. Czech. Chem. Comm., 24 (1959) 2172.
52 S. A. Selim, Ch. A. Philip and R. S. Mikhail, Thermochim. Acta, 36 (1980) 287.
53 N. Taniguchi and T. R. Ingraham, Can. J. Chem., 42 (1964) 2467.
54 F. Stander and C. P. J. Van Vuuren, Thermochim. Acta, 157 (1990) 357.

Zusammenfassung — Es wurde der Einfluß verschiedener experimenteller Bedingungen (z.B. Probenmasse, Atmosphäre, Aufheizgeschwindigkeit) auf die Zersetzung von NH_4VO_3, $CaCO_3$ und V_2O_5 untersucht. Die Ergebnisse zeigen eindeutig, daß Reaktionsweg und kinetische Parameter in Wirklichkeit nicht die einzelne Verbindung charakterisieren, sondern eher die Kombination von experimentellen Bedingungen und untersuchter Verbindung. Hierdurch ist es meistens unmöglich, "Standardbedingungen" zur Berechnung kinetischer Parameter zu wählen, da unter verschiedenen Umständen ganz andere Reaktionswege beschritten werden können.