ELSEVIER

Thermochimica Acta 388 (2002) 377–387

thermochimica acta

www.elsevier.com/locate/tca

Prediction of the progress of solid-state reactions under different temperature modes

B. Roduit*

AKTS, TECHNO-Pôle, CH-3960 Sierre, VS, Switzerland

Received 10 July 2001; received in revised form 9 November 2001; accepted 9 November 2001

Abstract

Using a computational method (AKTS-TA-Software) for solid-state kinetic analysis, the calculations of the progress of solid-state reactions were achieved employing temperature conditions different from those at which the experiments were carried out. The prediction of the solid-state reaction extent is illustrated by the results obtained during decomposition of hydromagnesite (component of some pharmaceuticals). The applied method was used for the prediction of the reaction progress under different temperature modes such as isothermal, non-isothermal, stepwise, adiabatic, modulated and, additionally for temperature profiles reflecting real atmospheric temperature changes. A comparison between calculated and experimental data is presented.

Keywords: Kinetic analysis; Thermal stability; Solids; Prediction of the extent of reaction; Temperature-modulated calorimetry

1. Introduction

Independent of the unsolved question of whether kinetic parameters of solid-state reactions have any real physical meaning, their usefulness for the quantitative description of kinetics of the process is fully accepted. This paper illustrates the application of the mathematical evaluation of the kinetic data for the prediction of the reaction extent under any temperature mode.

Over the last several years, research and development of new materials has accelerated significantly. This has resulted in increased interest in predicting their thermal stability both in extended temperature ranges and also under temperature conditions at which the investigation of their properties is very difficult to achieve. These difficulties are prevalent at low-temperatures (requiring very long scanning times), as well as under complex temperature profiles.

Model-fitting techniques can be effectively used to describe the solid-state reactions and predict the effect of the experimental parameters [1]. A full kinetic analysis of a solid-state reaction has at least three major stages: (1) experimental collection of data; (2) computation of kinetic parameters using the data from stage 1; and (3) predictions of the reaction progress for required temperature profiles applying determined kinetic parameters.

The solid-state reactions are often too complex to be described in terms of a single pair of Arrhenius parameters and the traditional set of reaction models [2]. As a general rule, solid-state reactions demonstrate profound multi-step characteristics. They can involve several processes with different activation

---

* Tel.: +41-848-800221; fax: +41-848-800222.
E-mail address: b.roduit@akts.com (B. Roduit).
URL: http://www.akts.com.

PII: S0040-6031(02)00052-7

energies and mechanisms. The method of the prediction of the summary reaction progress which considers only one kinetic parameter, namely the "activation energy" and ignores the others such as the pre-exponential factor and the model function, is an over simplification of reality. A reliable numerical technique applied in solid-state kinetics should be able to consider several activation energy values, pre-exponential factors and corresponding models for the description of the solid-state reaction extent. The correct choice of all the kinetic parameters strongly influences the ability to properly describe the progress of the reaction. The validity of approaches, which consider exclusively the activation energy values for the determination of the kinetic characteristics of solid-state reactions, can be hardly accepted [3].

Solid-state kinetic computations should be carried out with experimental data obtained at several (recommended not less than 5) heating rates (non-isothermal) or temperatures (isothermal) to ensure reliable results. Model-fitting methods that use single heating-rate experimental results should be avoided because they tend to produce highly ambiguous kinetic descriptions [3,4].

The data used for the prediction of the reaction extent should be collected under similar experimental conditions because the kinetic parameters of solid-state reactions are not intrinsic properties of an investigated compound and can change depending on the experimental conditions applied (PSTA-principle: parametric sensitivity of thermal analysis) [5].

Applying the results obtained by thermoanalytical techniques (such as TG, DTA (or DSC), TMA, EGA), a reliable numerical method should allow accurate prediction of the reaction progress of materials in a broad temperature range and under different temperature modes such as

- isothermal, non-isothermal and stepwise;
- modulated temperature or periodic temperature variations and rapid temperature increase (temperature shock);
- real atmospheric temperature profiles for investigating properties of low-temperature decomposed solids under different climates (yearly temperature profiles with daily minimal and maximal fluctuations);
- adiabatic (safety analysis).

The method applied in this paper can also be used for the elaboration of results obtained by hyphenated techniques such as TA–MS or TA–FTIR. The application of these techniques is widely recognized for the characterization of the degradation of solids [6]. In order to correctly apply the EGA-signals for the description of the kinetics of the decomposition of solids, the interrelation between thermoanalytical and mass spectrometric curves in the TA–MS or TA–FTIR system has to be known [7]. If the time lag between the thermoanalytical curve (e.g. DTG) and EGA-signal is negligible, the spectroscopic signal can be used not only for the qualitative and quantitative [8] analysis of the gaseous products but for the kinetic description of the process as well.

The application of the calculated kinetic parameters for prediction of the extent of the solid-state reactions will be illustrated by the examination of the extent of multi-stage decomposition of hydromagnesite (component of some pharmaceuticals) and simulated processes calculated for worldwide yearly temperature profiles. The potential application fields of the applied method include following subjects:

- Chemicals, pharmaceuticals and food.
- Material sciences, rubber, polymers.
- Metallurgy and ceramics.
- Catalysis, safety analysis, self-reactive chemicals and explosives.

2. Decomposition of hydromagnesite

2.1. Non-isothermal decomposition

The TG and DTA data collected during non-isothermal decomposition of the sample with a heating rate of 2.5, 5, 7.5, 10 and 15.5 K min^{-1} were used for the determination of the kinetic parameters used later for the prediction of the reaction extent. The sample was synthetic hydrated magnesium carbonate hydroxide (Merck p.a.) which XRD patterns and mass losses are in full agreement with the mineral hydromagnesite. The experimental conditions such as sample mass, atmosphere (He) and gas flow rate (50 ml min^{-1}) were identical in all experiments. In Figs. 1A, B and 2A and B, the experimental data of the TG and DTA-signals are presented and

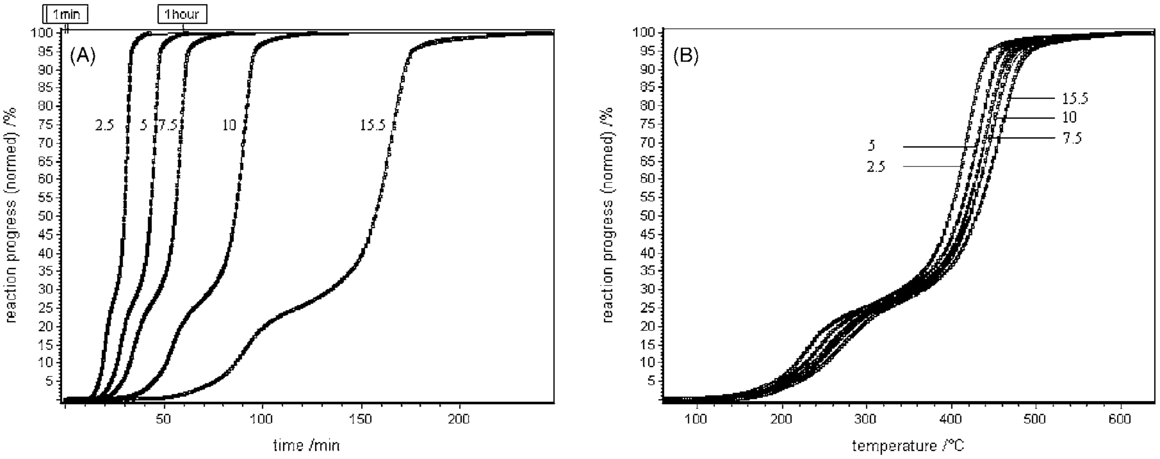

Fig. 1. Reaction extent (TG, normalized signals) α as a function of time (A) and temperature (B) for hydromagnesite decomposition under helium. Experimental data are represented as symbols, solid lines represent the calculated relationships α–t and α–T. The values of the heating rate in K min^{-1} are marked on the curves.

compared with the calculated curves of α–t and α–T. For each DTA scan, a tangential area-proportional baseline correction has been carried out. It is usually necessary to correct the measuring values of the baseline for all differential signal types, like DTA and/or DSC measurements. This is especially necessary when the reaction is characterized by the large difference of the specific heats of substrate and product.

2.2. Verification of numerical computations

Verification of numerical computations can be readily achieved by graphical comparison of the reaction progress predictions with results of a subsequent analysis of examined material. It is essential that the verification runs be done under identical experimental conditions as those used for the calculations. Change of the experimental parameters such as, e.g.

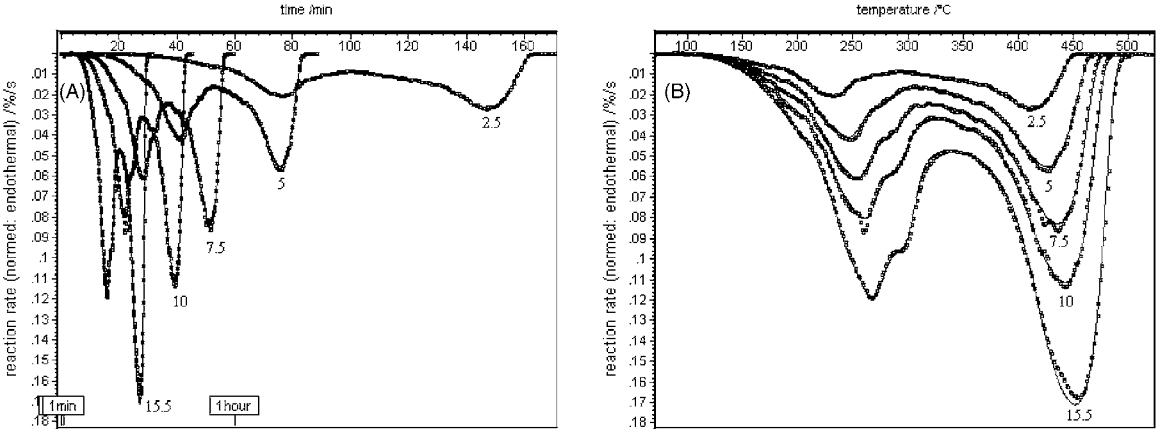

Fig. 2. Normalized DTA-signals as a function of time (A) and temperature (B) for hydromagnesite decomposition under helium. Experimental data are represented as symbols, solid lines represent the calculated relationships α–t and α–T. The values of the heating rate in K min^{-1} are marked on the curves.

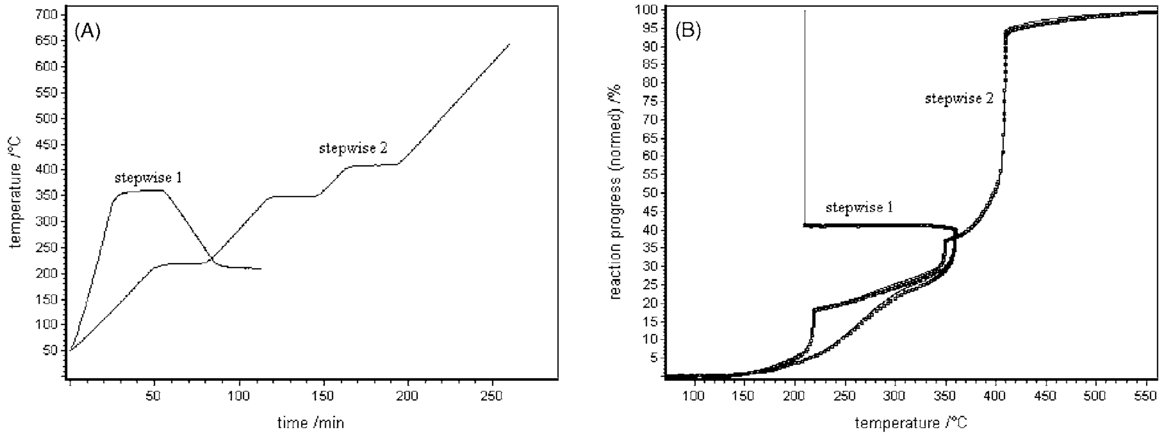

Fig. 3. (A) Temperature profiles involving isothermal and non-isothermal (heating and cooling) modes. (B) Corresponding reaction extent α of the decomposition are presented together with the reaction progress predictions of α–T. Experimental data are represented as symbols, solid lines represent the calculated relationships α–T. Accurate prediction of thermal stability is achieved.

sample mass, kind of the carrier gas and its flow rate, can considerably change the course of the thermoanalytical signals which, in turn, can distinctly influence the comparison of predictions with the experimental data. Predictions obtained are fully valid only for the experimental conditions applied in the thermoanalyzer and can vary when these conditions are changed [5]. The measured temperature profiles involving isothermal and non-isothermal (heating and cooling) modes are shown in Fig. 3A. In Fig. 3B, corresponding experimental data are presented together with the reaction progress predictions of α–T. The comparison between experimental and calculated reaction extents indicates that the presented multi-step model-fitting technique allows accurate prediction of the reaction course at the temperature mode chosen.

2.3. Cyclic temperature changes

The kinetic parameters calculated from the non-isothermal experiments allow prediction of the reaction progress at any temperature mode: isothermal, non-isothermal and intermediate intervals in the heating rate, expressed, e.g. in oscillatory temperature modes. The prediction of the reaction progress in oscillatory temperature mode (widely applied in temperature-modulated calorimetry [9,10]) is given in the subsequent sections.

In Fig. 4A, the arithmetic mean temperature (220 °C) of the oscillatory temperature modes is the same for all experiments, however, the differences in the amplitudes greatly influence the reaction progress (see Fig. 4B). The prediction of the decomposition of hydromagnesite at 220 °C with ±60 °C amplitude and 24 h period indicates that after 1 year the sample will be fully decomposed. For the same mean temperature (220 °C) and period (24 h) but different amplitudes (40, 20 and 0 °C for the isothermal conditions), hydromagnesite will decompose much less in this period of time (reaction extents are about 40, 35 and 32%, respectively). Total decompositions for the 40 and 20 °C amplitudes are reached within about 3 and 12 years whereas under isothermal conditions, about 25 years are required.

The calculations of the reaction rate of hydromagnesite decomposition in modulated temperature mode are presented in Fig. 5B. Fig. 5A depicts the applied temperature profile: starting temperature 5 °C, the underlying heating rate 2 °C min^{-1}, the modulation period 2 min, and the modulation amplitude ±15 °C. Temperature-modulated mode increases the basic understanding of the characterization of materials in different fields [11]. Presented results indicate that the prediction of some of the thermal characteristics under this mode is possible using conventional non-isothermal experiments.

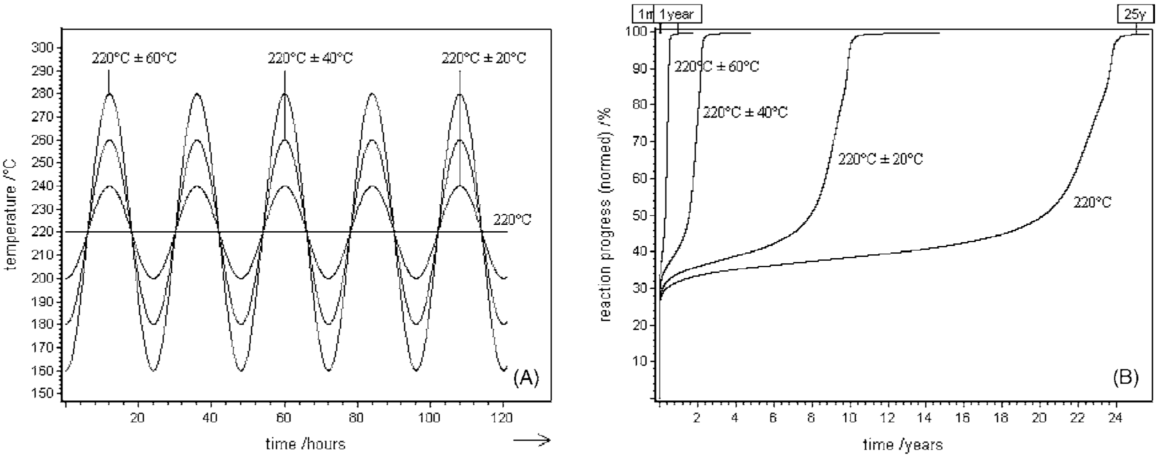

Fig. 4. (A) Temperature profiles in isothermal and oscillatory temperature modes (24 h period): (1) temperature variations 220 ± 60 °C; (2) temperature variations 220 ± 40 °C; (3) temperature variations 220 ± 20 °C; (4) isothermal 220 °C. (B) Corresponding reaction extent a of the decomposition of hydromagnesite in oscillatory temperature modes.

2.4. *Experimental procedure: isothermal or non-isothermal experiments?*

2.4.1. *Isothermal data*

Thermoanalytical measurements under isothermal conditions are usually investigated in a narrow temperature range due to experimental problems (particularly reaction times that are too short at high temperature or too long at low-temperature). Therefore, these measurements may not contain the necessary information, on the time–temperature dependence of a selected property, for the correct identification of the complexity of a process.

- Under isothermal conditions, one may be faced with an apparent kinetic system involving the contribution of one reaction only, whereas, under non-isothermal conditions, it would be necessary to consider several reactions. This is due to isothermal measurements being usually carried out over a

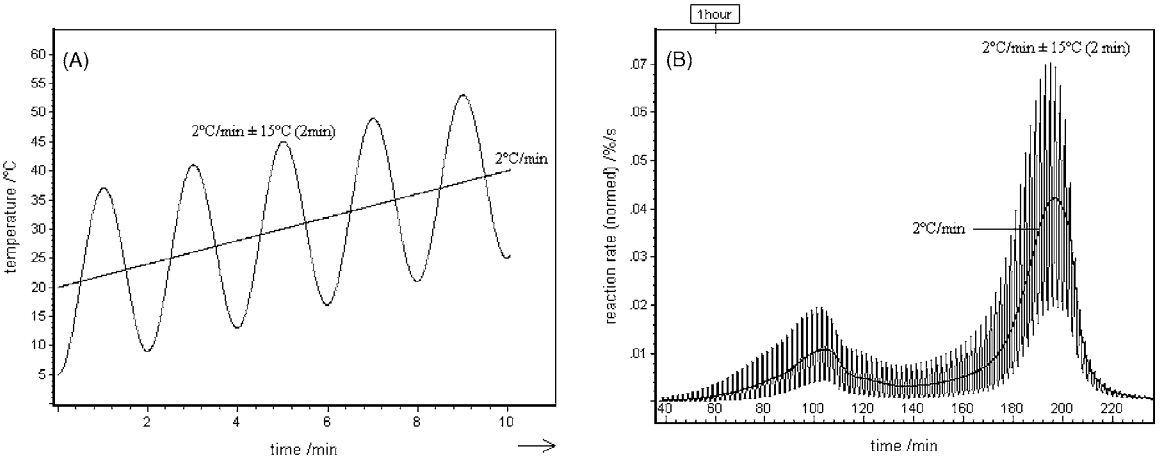

Fig. 5. (A) Temperature-modulated mode. (1) Underlying heating rate: 2 °C min^{-1}, modulation period: 2 min, modulation amplitude: ±15 °C; (2) non-isothermal: 2 °C min^{-1}. (B) Corresponding reaction rates of hydromagnesite decomposition (DTG expressed as normalized signals $d\alpha/dt$ time dependencies) under differing temperature modes.

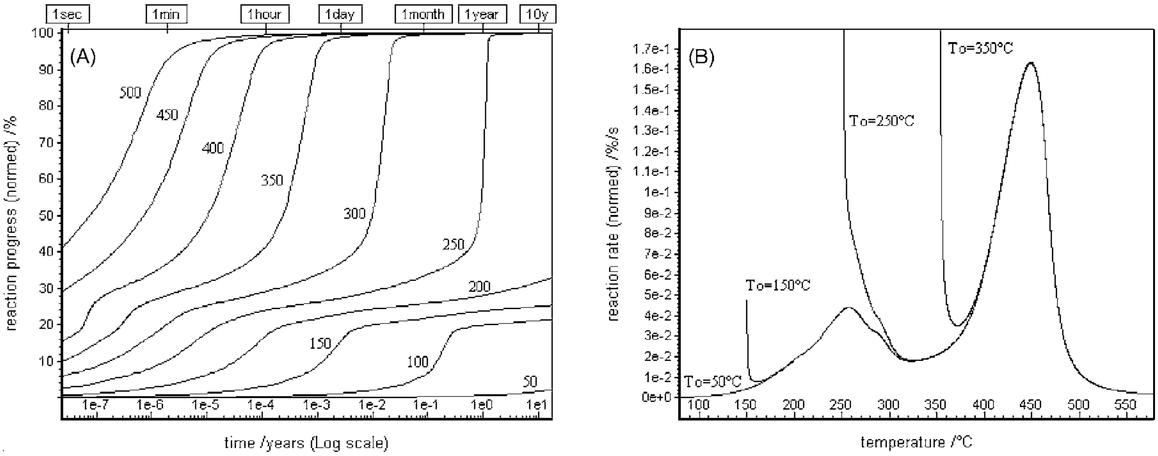

Fig. 6. (A) Extent of the decomposition of hydromagnesite under isothermal conditions. The values of the temperature (in °C) are marked on the curves. Isothermal experiments should be carried out at temperatures below 150 °C to avoid the occurrence of the temperature settling problem. However, investigation scanning times for such temperatures are just not practicable. (B) Simulated reaction rates (DTG, normalized signals $d\alpha/dt$) for a heating rate of 10 K min^{-1} with different starting temperatures $T_0 = 50$, 150, 250, 350 °C marked on curves.

narrow temperature range (generally 20–40 K) as compared to the non-isothermal experiments [3]. In such narrow temperature ranges, the isothermal reaction progress may be well described by using a single kinetic model not expressing the complexity of the total reaction process.

- Depending on the temperature window and type of reactions, truly isothermal conditions cannot be accomplished for very low and very high ranges of the reaction progress. The simulated curves for the decomposition of hydromagnesite under isothermal conditions presented in Fig. 6A clearly indicates the difficulties of the measurement of the α–t dependencies at the beginning of the decomposition. Isothermal experiments cannot be carried out at temperatures where the reaction rate is too fast and significant decomposition may occur during settling of the experimental temperature at the beginning of the experiments. For hydromagnesite, isothermal experiments should be carried out at temperatures below 150 °C (Fig. 6A) to avoid the influence of the temperature settling on the kinetic characteristics. Nevertheless, the time necessary to reach significant decomposition extent is not measurable from the experimental point of view (several years at temperatures below 150 °C to reach about 25% decomposition extent). To obtain reasonable scanning times (<24 h), temperatures above 350 °C should be chosen. However, at such temperatures, the problem related to the temperature settling occurs. Therefore, truly isothermal conditions cannot be accomplished and applied for the very low and very high ranges of the reaction progress α. This explains the difficulties of investigating thermoanalytical measurements under isothermal conditions and the choice of a narrow temperature range.

The above observations indicate that comparison of the kinetic parameters obtained under isothermal and non-isothermal conditions can be aggravated by unavoidable experimental phenomena that affect the kinetic data calculated from the isothermal conditions. In the isothermal temperature window, the maximum rate of decomposition usually occurs at the beginning of the reaction. At these temperatures, a reaction progress of a few percent is reached after a very short period of time, which clearly indicates the limitations of applications of very low α values in kinetic calculations for isothermal conditions. The solution is the determination of the kinetic parameters from non-isothermal experiments carried out over a wide temperature range. Non-isothermal experiments, starting with low-temperatures, suppress the temperature settling problem at the beginning of the reaction (see Fig. 6B) and consequently the limitations of measuring the

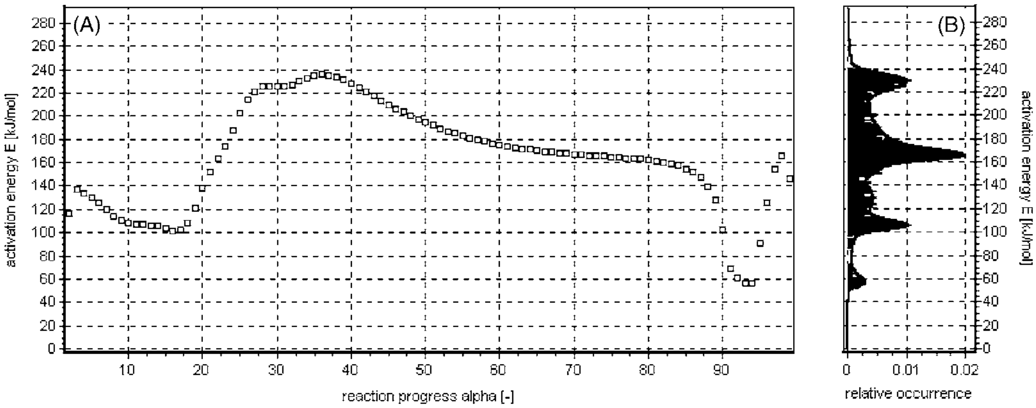

Fig. 7. (A) Reaction progress and activation energy. (B) Relative occurrence of the activation energy.

reaction progress under isothermal conditions. If the kinetic data are able to correctly describe the full temperature range, then they can be employed for the prediction of the isothermal reaction progresses taking place at temperatures lying inside the range of the non-isothermal experiments. This is especially important for multi-step processes which are accompanied by additional phenomena such as melting, polymorphic transformation, sublimation, etc. For such processes, the accurate mathematical transformation of isothermal data to non-isothermal data is impossible, whereas, the inverse procedure is feasible.

2.4.2. Non-isothermal data

In general, non-isothermal scans with different heating rates are carried out within a much wider temperature range than is possible, from the experimental point of view, in isothermal conditions. This allows discernment between the different reaction paths involved in the kinetic process because the data contain the necessary information on the time–temperature dependence of particular processes which is a prerequisite for the correct identification of the complex nature of the investigated reaction.

Computations are usually made with the results obtained from at least five heating rates. The application of heating rates too close to each other should be avoided. If they are very close, they become tantamount to a model-fitting analysis using single heating-rate methods. Consequently, they may fail the required purpose as amply reported in the literature [3,4].

The problem of the settling of the experimental temperature depends essentially on the kinetic characteristics of a reaction process and on the temperature at which the experiments under isothermal conditions are carried out [3]. The plot showing the change of the activation energy during hydromagnesite decomposition as a function of the reaction progress is presented in Fig. 7.

3. Calculation of adiabatic thermal transformation from non-isothermal DSC/DTA measurements

The calculation of adiabatic reaction progresses and/or explosion conditions from results of DSC/DTA measurements is often desirable because of the small amounts of material available. The precise prediction of such reaction progresses may be required in the safety analysis of many technological processes. Calculations of an adiabatic temperature–time curve of the reaction progress can be also used to determine the decrease of the thermal stability of materials during storage at temperatures near the temperature of the beginning of the reaction. Due to insufficient thermal convection and limited thermal conductivity, a progressive temperature increase in the sample can easily take place, resulting in a thermal explosion.

Several methods have been presented for prediction of the reaction progress of exothermic reactions under adiabatic conditions [12–15]. However, because

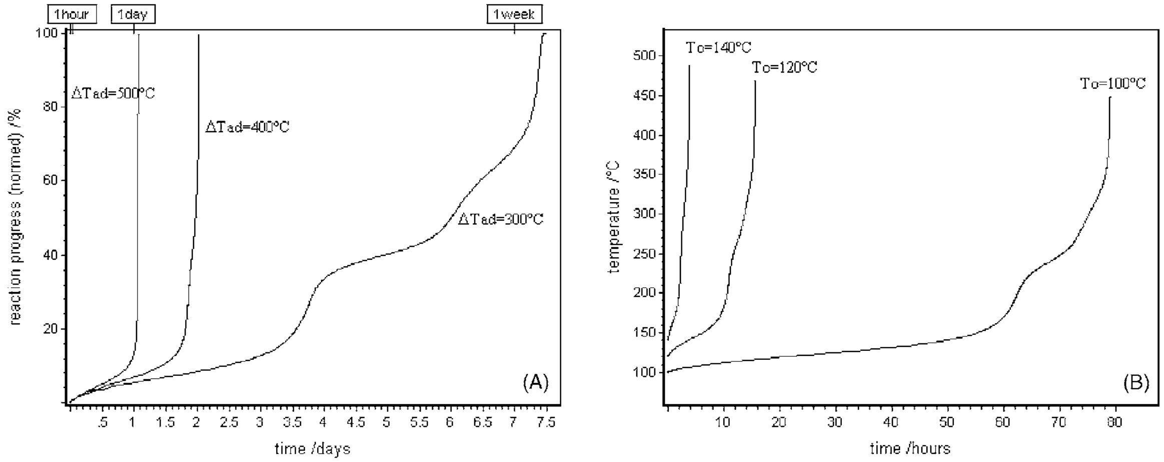

Fig. 8. Hypothetical reaction process, being identical as hydromagnesite decomposition but exothermic. (A) Simulated α–t relationships with a starting temperature of 100 °C for three different $\Delta T_{ad} = \Delta H_r/c_p = 300$, 400 and 500 °C (marked on curves). (B) Calculations of the adiabatic self-heating reaction determined for several starting temperatures $T_0 = 100$, 120 and 140 °C (marked on curves) with $\Delta T_{ad} = 350$ °C. Depending on the ΔT_{ad} considered, the choice of the starting temperatures strongly influences the adiabatic induction time.

solid-state reactions usually have a multi-step nature, the accurate determination of kinetic characteristics strongly influences the ability to correctly describe the progress of the reaction. For adiabatic self-heating reactions, incorrect kinetic description of the process is usually the main source of serious errors in its interpretation. The decomposition of hydromagnesite is a complex endothermal process (see Fig. 2A and B). For illustration, let us consider the reaction progress of a hypothetical process, being identical to hydromagnesite decomposition but exothermic. Using the reaction heat (ΔH_r) and the heat capacity (c_p), one can calculate the reaction progress due to self-heating for different values of ΔT_{ad} (with $\Delta T_{ad} = \Delta H_r/c_p$). In Fig. 8A, the simulated α–t relationships with a starting temperature of 100 °C are presented for three different ΔT_{ad} (300, 400 and 500 °C). Calculations of the temperature progress of adiabatic self-heating reactions for several starting temperatures (100, 120 and 140 °C with $\Delta T_{ad} = 350$ °C) are presented in Fig. 8B. The adiabatic induction time is defined as the time which is needed for self-heating from the start temperature to the time of maximum rate. Depending on the ΔT_{ad} considered, the choice of the starting temperatures strongly influences the adiabatic induction time and, therefore, the boundary conditions valid for achieving necessary safety, e.g. storage of self-reactive substances.

4. Prediction of the reaction progress under temperature mode corresponding to real atmospheric temperature changes

The important goal for investigating the kinetics of thermal decompositions of solids is the need to determine the thermal stability of substances, i.e. the temperature range over which a substance does not decompose at an appreciable rate. The correct prediction of the reaction progress of unstable materials under ambient conditions (food, drugs, some polymers, etc.) requires accurate application in the calculations of both:

- the kinetic parameters;
- the exact temperature profile for a given climate.

4.1. Influence of the kinetic parameters on the reaction extent occurring under certain real temperature profiles

Let us consider the influence of the real temperature profile of Las Vegas (Nevada, USA) on the course of three simulated reactions that obey the same reaction model (first-order reaction), have identical pre-exponential factors ($A = 1E{+}10\ s^{-1}$), but different activation energies ($E_{a1} = 100\ kJ\ mol^{-1}$, $E_{a2} = 105\ kJ\ mol^{-1}$, $E_{a3} = 110\ kJ\ mol^{-1}$). The simulated curves of the α–T dependencies for a heating rate of $10\ K\ min^{-1}$

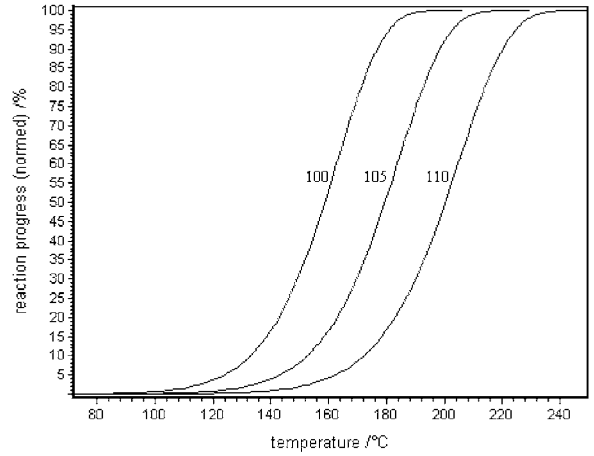

Fig. 9. Simulated α–t relationships for different kinetic triplets calculated for a heating rate of 10 K min^{-1}. Three reactions obey the same reaction model (first-order reaction), have identical pre-exponential factors ($A = 1\text{E}+10\ \text{s}^{-1}$), but have different activation energies ($E_{a1} = 100$ kJ mol^{-1}, $E_{a2} = 105$ kJ mol^{-1}, $E_{a3} = 110$ kJ mol^{-1}). The values of the activation energy in kJ mol^{-1} are marked on the curves.

are presented in Fig. 9 for the three different cases. By applying the above kinetic parameters for calculations, the three simulated reaction progresses can be determined for the real temperature profile of Las Vegas presented in Fig. 10A. The temperature profile is the average of all daily minimal and maximal temperatures recorded for each day of the year between the years 1961 and 1990. The temperature fluctuations of this 30 year daily temperature summary will be repeatedly applied in the calculations for the examination of the thermal properties with cyclic temperature changes over the years. Fig. 10B presents a zoom of the temperature profile of Las Vegas with daily minimal and maximal temperatures from 1 to 31 January (30 year daily temperature summary). The α–t dependencies in Fig. 11A illustrate the reaction progress of three simulated reactions for several years in Las Vegas. Results of the calculations for the reaction with $E_{a1} = 100$ kJ mol^{-1} indicate that after 5 years, the reaction will be fully completed. Reactions 2 and 3 with respectively $E_{a2} = 105$ kJ mol^{-1} and $E_{a3} = 110$ kJ mol^{-1} will progress much less in this period of time (transformation progresses are about 50 and 10%, respectively).

4.2. Influence of the temperature profile changes on the reaction extent

Let us apply the following kinetic triplet (reaction model: first-order reaction, pre-exponential factors: $A = 1\text{E}+10\ \text{s}^{-1}$, activation energy: $E_a = 100$ kJ mol^{-1}) for the prediction of solid state reaction extent in Las Vegas, Seattle and Nome (Alaska, USA) (Fig. 11B). It can be seen that within 5 years, the reaction is completed in Las Vegas, whereas, in Seattle and Nome, the degree of the decomposition amounts to about 65 and 18%, respectively. In Fig. 12, the same temperature profiles were used for the calculation of the thermal stability of hydromagnesite. Hydromagnesite exposed to daily temperature changes in these three places decomposes only slightly (<1%) after 25 years.

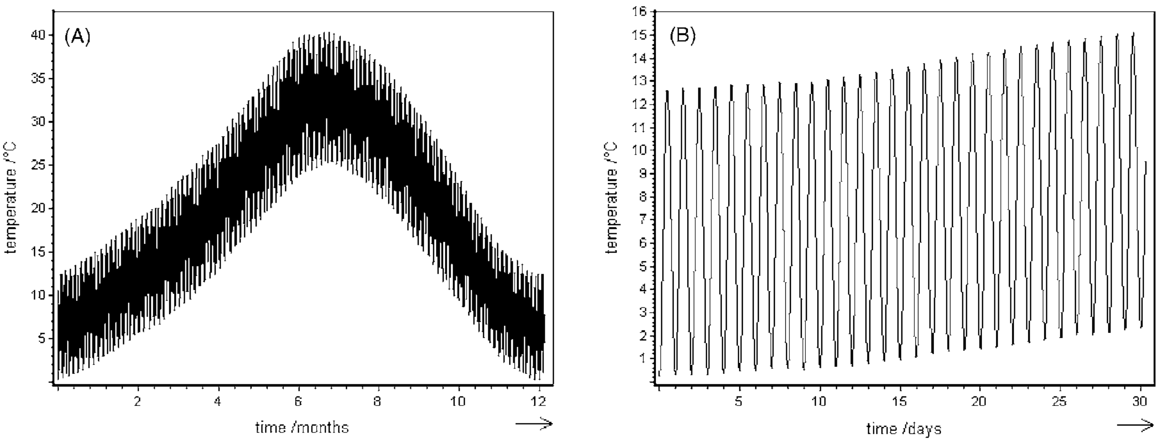

Fig. 10. (A) Average minimal and maximal temperatures recorded for each day of the year between the years 1961 and 1990. (B) Zoom of the temperature profile of Las Vegas with daily minimal and maximal temperatures from 1 to 31 January (average of 30 years).

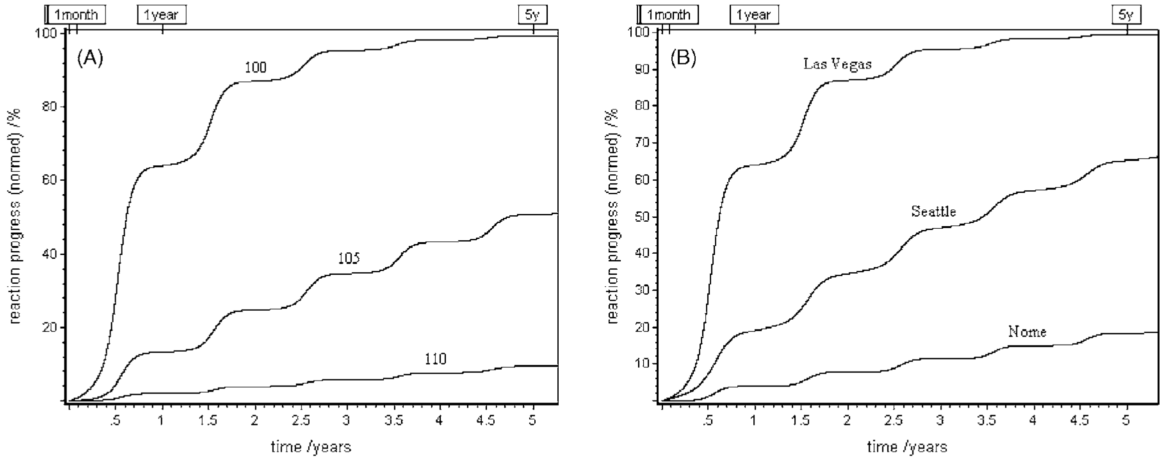

Fig. 11. (A) Predictions of the transformation progress of three hypothetical reactions for the Las Vegas temperature profile. The three reactions obey the same reaction model (first-order reaction), have identical pre-exponential factors ($A = 1E{+}10\ s^{-1}$), but have different activation energies ($E_{a1} = 100\ kJ\ mol^{-1}$, $E_{a2} = 105\ kJ\ mol^{-1}$, $E_{a3} = 110\ kJ\ mol^{-1}$). The values of the activation energy in kJ mol^{-1} are marked on the curves. (B) Predictions of the transformation progress of a hypothetical reaction for the Las Vegas, Seattle and Nome (Alaska) temperature profiles. Kinetic triplet: model (first-order reaction), pre-exponential factors ($A = 1E{+}10\ s^{-1}$), activation energy ($E_a = 100\ kJ\ mol^{-1}$).

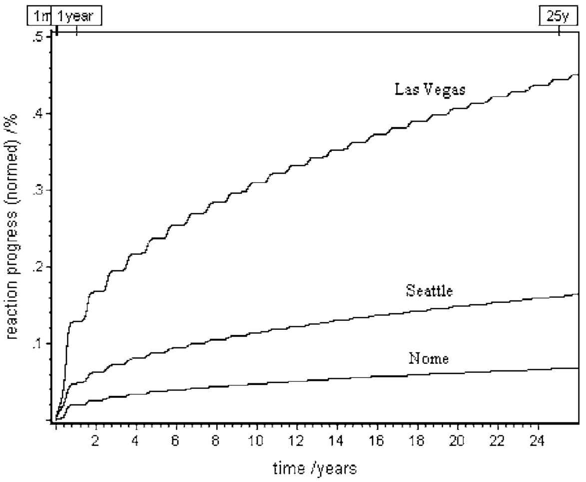

Fig. 12. Predictions of the extent of hydromagnesite decomposition for the Las Vegas, Seattle and Nome (Alaska) temperature profiles. The hydromagnesite exposed to daily temperature changes decomposes less than 1% after 25 years.

5. Conclusions

Using the AKTS-TA-Software, calculations of complex reaction progresses were carried out for temperature conditions at which the collection of data is very difficult from the experimental point of view. Solid-state reactions are often too complex to be described in terms of a single pair of Arrhenius parameters and a simplified set of reaction models. An accurate description of decomposition kinetics and a high fit quality are the basic conditions for predictions possessing an acceptable degree of confidence. Adequate predictive examination of the investigated reactions requires at least five thermoanalytical measurements carried out with different heating rates, generally in the range of 1–20 K min^{-1}. The scans obtained by any thermal technique (such as e.g. TG, DTA, DSC, EGA, TMA), can be applied for the calculations. The data should be collected under similar experimental conditions because the kinetic parameters of solid-state reactions are not intrinsic properties of an investigated compound but can change depending on the experimental conditions applied. The experimental data set used for calculations must contain the whole information on the time–temperature dependence of a selected property. The complexity of the process is more easily detectable for non-isothermal data, but might not clearly show up in isothermal experiments because of the narrower temperature window applied. Calculations can be achieved for any fluctuation of the temperature, which makes possible the predictions of thermal stability properties for varying climates. Exact consideration in the calculations of daily minimal and maximal temperature variations of worldwide climates provides very valuable insight when interpreting and quantifying the reaction progress of materials subjected to atmospheric conditions. For safety analysis examinations, the determination of the critical starting temperatures, development of the temperatures and adiabatic induction times are important parameters both for the production as well as for the storage of potentially explosive materials.

Acknowledgements

The author would like to thank Prof. F. Stoessel (Swiss Federal Institute of Technology, EPFL, CH-1015 Lausanne and Institute of Safety and Security, SWISSI, CH-4002 Basel, Switzerland) for fruitful discussions concerning the adiabatic transformations.

References

[1] B. Roduit, Thermochim. Acta 355 (2000) 171.
[2] M.E. Brown, M. Maciejewski, S. Vyazovkin, R. Nomen, J. Sempere, A. Burnham, J. Opfermann, R. Strey, H.L. Anderson, A. Kemmler, R. Keuleers, J. Janssens, H.O. Desseyn, C.-R. Li, B. Tang, B. Roduit, J. Malek, T. Mitsuhashi, Thermochim. Acta 355 (2000) 125.
[3] M. Maciejewski, Thermochim. Acta 355 (2000) 145.
[4] M. Criado, A. Ortega, F. Gotor, Thermochim. Acta 157 (1990) 171.
[5] B. Roduit, M. Maciejewski, A. Baiker, Thermochim. Acta 282/283 (1996) 101.
[6] K.G.H. Raemaekers, J.C.J. Bart, Thermochim. Acta 295 (1997) 1.
[7] B. Roduit, J. Baldyga, M. Maciejewski, A. Baiker, Thermochim. Acta 295 (1997) 59.
[8] M. Maciejewski, C.A. Müller, R. Tschan, W.-D. Emmerich, A. Baiker, Thermochim. Acta 295 (1997) 167.
[9] B. Wunderlich, Thermochim. Acta 355 (2000) 43.
[10] M. Reading, D. Elliott, V.L. Hill, J. Therm. Anal. 40 (1993) 949.
[11] T. Ozawa, Thermochim. Acta 355 (2000) 35.
[12] P.H. Thomas, Trans. Faraday Soc. 54 (1942) 60.
[13] N. Semenov, Einige Probleme der chemischen Kinetik und Reaktionsfähigkeit, Akademieverlag, Berlin, 1961.
[14] D.A. Frank-Kamenetskii, Diffusion and Heat Transfer in Chemical Kinetics, Plenum Press, New York, 1969.
[15] T. Grewer, Thermochim. Acta 225 (1993) 165.