

**Kinetics of consecutive reactions in the solid state:  
Thermal decomposition of oxalates.**

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**Abstract**

The thermal and kinetic aspects of solid state decomposition reactions can be complex and possess a large number of parameters to investigate. The determination of the activation energies for the several intermediates in the thermal decomposition is particularly sensitive to the overlap in thermal decomposition traces. To overcome this problem we have undertaken the detailed kinetic analysis of the well-known thermal decomposition of calcium and strontium oxalates and mixtures of both. Indeed, their small difference in decomposition temperatures, from oxalate to carbonate, allowed us to simulate overlapping TGA signals and to use these data to test the validity of the experimental conditions and mathematical methods used to derive calculated kinetic values.

**Key-words:** thermal analysis, kinetics, solid state reactions, mathematical processing of data.

**1. Introduction**

Knowledge of kinetic parameters, such as the reaction rate and activation energy, is one of the keys to determine the reaction mechanisms in solid phases. When changes in the mechanisms are observed, this can lead to a unique characteristic and hence a better knowledge of the materials.

Besides this, there are also more practical reasons to know the reaction rates and their temperature dependence. The industry needs measurements of those parameters for the accurate design of installations and treatment conditions, because augmentation of temperature or elongation of reaction time means more costs. Using an appropriate mathematical expression, the TA-experiments can be applied for the modeling of industrial thermal processes. The results of the kinetic investigation of thermoanalytical reactions in the solid state can also be applied to problems as useful lifetime of certain components, oxidative and thermal stability and quality control.

During our prior thermoanalytical studies of the decomposition kinetics of nitrate precursors for the synthesis of ceramic high temperature superconductors (HTSC) we were confronted with the ubiquitous presence of consecutive reactions in the solid state. Although spray drying of aqueous nitrate solutions was demonstrated to result in very reactive precursor materials, the determination of activation energies for the several intermediates in the thermal decomposition is particularly sensitive to the overlap in thermal decomposition traces. The thermal and kinetic aspects of these decompositions are complex and possess a large number of parameters to investigate.

## 2. Subject and Methods

To overcome the problems concerning the overlap of consecutive reactions we have undertaken the detailed kinetic analysis of the well-known thermal decomposition of calcium and strontium oxalates and mixtures of both. Indeed, their small difference in decomposition temperatures, from oxalate to carbonate, allowed us to simulate overlapping TGA signals and use these data to test the validity of the experimental conditions and mathematical methods used to derive calculated kinetic values.

In order to obtain the highest quality values for kinetic parameters from thermal analysis (TA) data, the combined use of simultaneous thermogravimetric and differential thermal analysis (TGA-DTA), evolved gas analysis by mass spectrometry (EGA-MS), high temperature X-ray diffractometry (HT-XRD)\* and thermomicroscopy (TM) is advocated.

Thermal analysis is defined as [1]: a group of techniques in which a property of the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed. TGA is a technique in which the *mass* of the sample is monitored, while DTA monitors the *difference in temperature* between the sample and a reference material. EGA is a technique in which the nature and/or the amount of gas or vapor evolved from the sample is monitored, by MS in our case. An even more adequate technique is the direct identification of the (intermediate) decomposition products by HT-XRD\*. And last but not least thermomicroscopy (TM), by means of an optical metallurgical polarizing microscope equipped with heating stage, is indispensable in the study of solid state kinetics. It is essential to interpret observations with due consideration of the possibility that the material may undergo a loss of structural order at elevated temperature, i.e. melting [2]. TM observations are also required to supplement conventional kinetic data in the formulation or determination of a reaction mechanism or reaction model [3]. Such model is needed in the mathematical model fitting methods to calculate the kinetic parameters (see below).

Several mathematical methods are compared for calculating the kinetic parameters of solid state reactions: isothermal and non-isothermal, model fitting and model-free methods.

The kinetic parameters of thermal decomposition reactions of some oxalates, i.e. the activation energy  $E$ , pre-exponential factor  $A$  and reaction model  $f(\alpha)$ , were determined under *isothermal* and *non-isothermal* conditions. The mathematical methods to process the TA data can be divided into *model fitting* and *model-free* methods. The model fitting approach has the advantage that only one TA measurement is needed. However it suffers from an inability to determine the reaction model uniquely [4]. In spite of this unreliability, it's a quick method to become a first indication of possible values for the kinetic parameters.

The alternative model-free methodology is based on the isoconversional principle. The use of these methods helps to avoid the problems that originate from the ambiguous evaluation of the reaction model. The model-free methodology allows the determination of the dependence of the activation energy on the extent of conversion and permits reliable mechanistic conclusions to be drawn [4]. A negative aspect is the need for at least 3 TA experiments what makes it more time consuming.

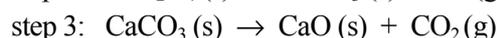
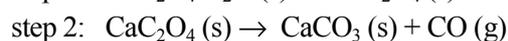
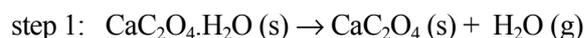
We also simulated the thermal decomposition reactions with the stochastic simulation package CKS (Chemical Kinetics Simulator). After the input of the sequence of consecutive reactions in conventional chemical notation, the calculated kinetic parameters for each step, and the run conditions, CKS simulates the changes in the system by randomly selecting among the reaction steps and using probabilities derived from rate laws for each step in the mechanism.

### 3. Results

The solid state reactions we have studied are the thermal decomposition reactions of calcium- and strontium oxalates and their mixtures. The  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  was synthesized by a precipitation reaction.  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  water based solutions were brought together dropwise under continuous stirring followed by the  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  precipitation. The  $\text{SrC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ , i.e. a mixture of  $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  and  $\text{SrC}_2\text{O}_4 \cdot 2,5\text{H}_2\text{O}$  according to X-ray powder diffractometric characterization, was synthesized in a similar way with a  $\text{Sr}(\text{NO}_3)_2$  solution. We also made mechanical 1/1 and 1/2 mixtures of the  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  and  $\text{SrC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$  powders.

Finally,  $\text{Ca}_x\text{Sr}_{1-x}\text{C}_2\text{O}_4 \cdot y\text{H}_2\text{O}$  solid solutions were synthesized by bringing together the three solutions dropwise under continuous stirring to co-precipitate. The obtained results were compared with the mechanical mixtures. Finally we are also planning to spray dry mixtures of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  and  $\text{SrC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$  to achieve an intermediate situation.

During the thermal decomposition of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  there are three reaction steps visible at increasing temperature, corresponding to the loss of  $\text{H}_2\text{O}$ ,  $\text{CO}$  and  $\text{CO}_2$ , respectively:



The thermal decomposition of  $\text{SrC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$  is similar to that of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  with these remarks:

- The dehydration takes places in two consecutive steps.
- The following consecutive decomposition steps of the oxalate and carbonate occur at higher temperatures.

The small difference in decomposition temperatures (figure 1 left) for the decomposition of these oxalates to the respective carbonates allowed us to simulate overlapping TGA-signals by mechanically mixing (1/1 mixture) the oxalates of calcium and strontium and to compare the extracted kinetic parameters with those from the individual oxalates (figure 1 right).

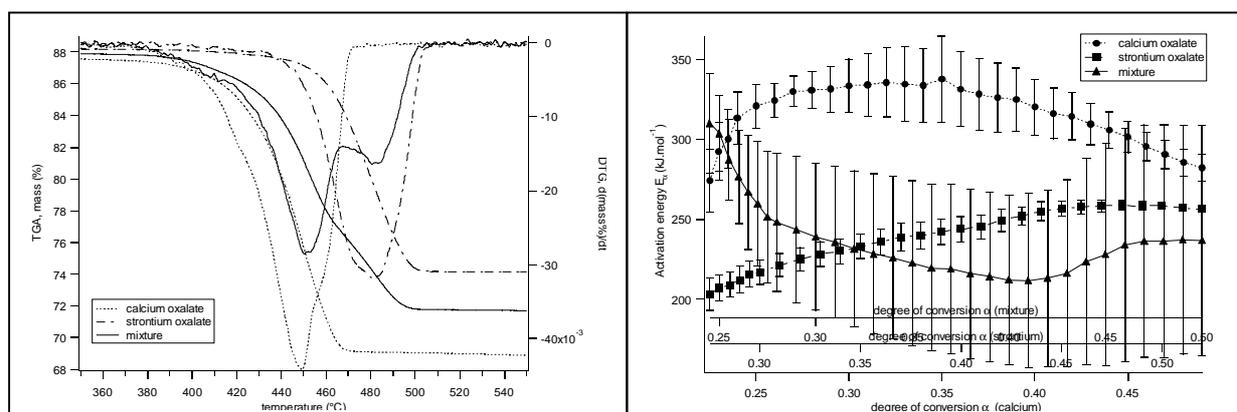


Figure 1: TGA (5°C/min, dynamic  $\text{N}_2$ -atmosphere) and DTG signals (left) and the dependence of activation energy on the extent of conversion (right) for the decomposition of the oxalates to the respective carbonates.

The dependence of the activation energy on the extent of conversion for the decomposition of the oxalate mixture (triangles) is not yet fully understood. In the first half of the curve the value of  $E_{\alpha}$  decreases, what can be understood because the fraction of decomposing strontium oxalate, which has a smaller activation energy than calcium oxalate, will increase. The second half of the curve, i.e. the decrease of  $E_{\alpha, \text{mixture}}$  below values of  $E_{\alpha, \text{strontium oxalate}}$ , can't be explained up till now.

The more reliable “model-free” kinetic parameters, calculated with the model-free methods, were entered in the stochastic simulation package CKS and the simulated TGA-traces of the decompositions were in good agreement with the measured TGA-traces.

#### 4. Discussion / Conclusions

These individual and mixed oxalates allowed us to understand the dependence of the activation energy on the extent of conversion and to extract reliable kinetic parameters which were in good agreement with the literature.

In correspondence to [4], the use of slow heating rates allows one to narrow the temperature range of a non-isothermal experiment and this may help to conduct the isothermal and non-isothermal experiments over comparable ranges of temperatures and to reduce the quantitative difference between the dependencies of the activation energy on the extent of conversion derived from isothermal and non-isothermal experiments.

The overlap in thermal decomposition traces can result in large variations of the activation energy with the extent of conversion. The degree of overlap and thus, the dependence of the activation energy on the extent of conversion can be influenced by altering the experimental conditions of the measurements, e.g. heating rates, partial pressure of reactive atmospheric components.

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