Round robin test on the kinetic evaluation of a complex solid state reaction from 13 European laboratories. Part 2. Kinetic DSC-analysis

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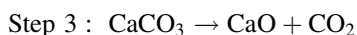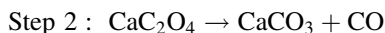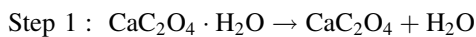[b]*Department of Calorimetry, University of Ulm, PO Box 4066, D-89069, Ulm, Germany*

Abstract

In 1994 the decomposition of calciumoxalate monohydrate as a three-step reaction has been investigated by 13 labs using DSC-method. Starting from one identical point all files with the results have been evaluated by objective kinetics by the authors. The evaluation has been performed using a well proved non-linear optimization method. 96 DSC-data sets have been evaluated kinetically several times. The results were analyzed critically on the basis of real model concepts for the course of the dehydration, the CO-split off and of the CO_2-split off, respectively. The results allow an optimistic assessment for the application of kinetic procedures to solid state reactions with well-known chemical course investigated by DSC. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

In the first part of the interlaboratory round robin test (RRT), initiated by the kinetic group of the GEFTA, the thermo gravimetry (TG)-data sets have been evaluated and compared [1]. The decomposition of calciumoxalate monohydrate represents a three-step reaction according to the reactions given below.

$$\text{Step 1}: \ CaC_2O_4 \cdot H_2O \rightarrow CaC_2O_4 + H_2O$$

$$\text{Step 2}: \ CaC_2O_4 \rightarrow CaCO_3 + CO$$

$$\text{Step 3}: \ CaCO_3 \rightarrow CaO + CO_2$$

The aim of the RRT was to examine the possibility of DSC-conditions to obtain reproducible data with different commercial devices, to check the critical optimism and to determine the essential conditions for satisfactory kinetic data analysis. Because nearly all involved labs have delivered data sets not only from DSC but also from TG-part [1] the DSC-data sets have been converted to the ASCII format again to guarantee an equivalent treatment of all results without changing or influencing the data character themselves. The mathematical evaluation has been performed by the Anderson group in Greifswald using the known software package TA-kin [2].

In case of the second reaction step the DSC-method may be used as an indicator for more or less oxidation of the carbon monoxide to carbon dioxide which is one reason for the uncertainty within the kinetic evaluation. But this problem can be minimized by correct processing.

The common consideration about linear and non-linear evaluations of data sets of the TA can be

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completely borrowed from part 1 of this paper [1]. However, in general the non-linear mathematical procedures and their automatic application show decisively advantages for practical evaluations.

2. Special remarks on the DSC evaluation

In comparison to the TG-measurements the evaluation of DSC-files is complicated by heat exchanges between sensor and sample which differs from apparatus to apparatus and cannot be defined exactly. The heat flow influences not only the temperature profile across the sample but also the obtained heat flow signal itself. Thus the measured curve is influenced by several factors, such as the construction of the DSC-device, the type and material of the applied crucibles and the sample mass. As each factor of influence has its own temperature dependence, the sum of these effects results in a non-linear baseline. In many cases it is not possible to get the proper baseline by using the data of a second measurement with the reacted sample. Because of this problems the separated single reaction steps have been provided with separate linear baselines (application of the program part CUT of TA-kin). Sigmoidal baselines have been discussed in the literature to consider the change of

heat capacity of the sample during a chemical reaction. But such types of corrections were not used for the evaluation of the DSC-measurements of the RRT.

For the CO-split off the problem of the oxidation of carbon monoxide under air may arise. This can result in a dramatic consequence for measurements in air, because the CO-split off causes originally an endothermic signal whereas the signal of the oxidation is exothermic. Thus the signal decreases with increasing oxygen concentration of the environmental atmosphere and changes its sign.

To evaluate all data sets in spite of this problems in a comparable way, we calculated conversion versus time curves from the delivered heat flow curves:

$$\alpha(t) = \frac{\int_0^t p(t)\,\mathrm{d}t}{\int_0^\infty p(t)\,\mathrm{d}t},$$

p . . . heat flow or proportional signal.

The obtained α–t curves enable unified kinetic evaluations of all considered DSC-measurements of the RRT independent from the effective atmosphere. Using the conversion value α limitates the evaluation to reaction models with a single conversion value. Fig. 1 shows some real measured curves. The irregularities in the start region of the second reaction step
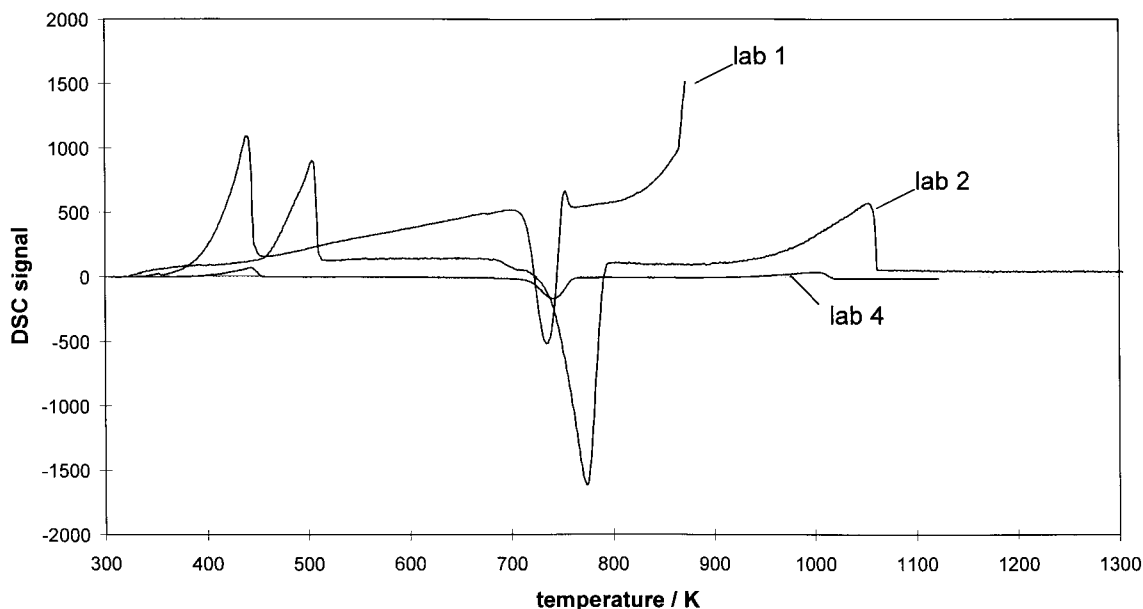

Fig. 1. Direct comparison of measured curves from three different labs representing the great differences of the experimental conditions.

Table 1
The temperatures of maximum rate of conversion for all reaction steps in inertia and air atmosphere

Inertia				Air			
Lab	Step 1	Step 2	Step 3	Lab	Step 1	Step 2	Step 3
1 K min^{-1}							
1	147	457		1	146	447	
2/1	177		688	2/1	209	473	722
2/2	199	495	719	2/2	209	477	739
4	176			3	148	464	717
6	143	459		4	140	449	675
8	185	479		5	175	444	
10	144	441					
Average	167	466	704		171	459	713
Standard deviation	22	21	22		32	14	27
3 K min^{-1}							
1	166	475		1	166	463	
2/1	201	505	746	2/1	231	493	774
2/2	226	510	783	2/2	321	501	781
4	170	478		3	191	526	827
6	183	482		4	171	469	729
8	219	501		5	189	468	
10	158	466					
Average	189	488	765		212	487	778
Standard deviation	27	17	26		58	25	40
10 K min^{-1}							
1	190	497		1	190	487	
2/1	246	535	790	2/1	279	524	827
2/2	271	544	836	2/2	269	527	834
4	206	503		3	234	547	846
6	214	501		4	207	492	778
8	238	533		5	202	489	
10	180	495					
Average	221	515	813		230	511	821
Standard deviation	32	21	33		37	25	30

The standard deviations of these temperatures (at the same heating rate) reflects the effect of the different experimental conditions for the involved labs.

can be explained as an additional process step. The consideration of this process during the evaluation would necessitate a complex reaction model. But such complex models were not used within the RRT. At first, complex kinetic models should be avoided due to the chosen kind of evaluation (α–t curves). Second, the measured curves does not contain sufficient information for a safe determination of all kinetic parameters of such a complex model. Actually the evaluation of the single curves shows that the correlation between E_A and ln k_0 even for a single reaction step could not be clarified completely (mathematical minimization problems) [3,4]. The measured curves of different labs show considerable differences. This is demonstrated in Table 1 by the represented temperature at maximum conversion speed.

3. Choice of reaction

The above mentioned three-step reaction has been chosen because of

- the well-known chemistry of each single step,
- the simple *grating* processes in comparison to many other solid state reactions.
- The possibility to separate the single steps from the data files.

The DSC-measurements of all labs are comparable because of

- the same sample mass about 10 mg,
- the same heating rates of 1, 3 and 10 K min^{-1},
- a defined atmosphere: air oxygen or inertia (N_2, He, Ar), respectively.

4. DSC of the thermal decomposition of calciumoxalate monohydrate

The ASCII files delivered by the participants have been unified and coded before kinetic evaluation. The temperature area of each step varies dependent on the chosen heating rate and atmosphere. Eight of the 13 labs delivered DSC-measurements (two of them only in air, three only in inertia). The third reaction step has been investigated by only three labs because of the high temperatures. The temperatures at the maximum conversion speed differ between the labs by 30–100 K depending on the heating rate. The standard deviations in Table 1 distinct differences in the first and third decomposition step. Unlike the TG-part of the RRT there is no significant relation to the used atmosphere.

Fig. 1 summarized results from three arbitrary chosen labs. Depending on the used DSC-equipment two or three peaks were found. A direct correspondence between the curves cannot be seen. The great differences between the curves of the single labs appear in Figs. 2–4. But these deviations do not hinder the quantitative kinetic comparison of all data files.

5. Kinetic evaluation

5.1. Step 1: H$_2$O-split off

For the second step, the removal of water, 39 measurements have been send in and lead to 78 single and nine overall-evaluations. The results of the kinetic

evaluations are based on the model of a two-dimensional phase-boundary reaction R2. In Table 2 for inertia and Table 3 for air atmosphere 13 groups of DSC-files of different heating rates are shown. The observations at inertia atmosphere gave deviations of the kinetic rate constant k at 150°C of more than one magnitude. Whereas the activation parameters, within one group, are relatively similar, however, the differences of the activation energies between the labs are in the range of 20 kJ mol^{-1}.

The so-called compensation plot (Fig. 5) shows a distinct correlation between E_A and ln k_0. This effect is caused by the mathematical structure of the Arrhenius equation and must be expected in every case but to a different extent.

As for the thermogravimetric investigations the results can be unified by single parameter evaluations using the average of the ln k_0-values obtained from the single-evaluations (Table 3, column 3). The E_A values, corresponding to the average value of ln k_0=22.17, are listed in the last column. All together we get a group of results which could be called satisfactory, if we take, again, the different experimental conditions of the involved labs into consideration. It can be observed, however, that DSC-measurements can be used too for the kinetic characterization of this dehydration process.

Table 3 includes the evaluations of the dehydration in air. As in the inertia case the measured curves have been investigated by single-evaluation and overall-evaluation, respectively, of curves from the same lab but at different heating rates. In general it can be pointed out that agreement within single labs cannot be observed in the same quality as in Table 2. This is an indication for problems due to the stabilization of the experimental conditions under air. The compensation plot (see Fig. 6) shows a stronger scatter than before (Fig. 5) but the correlation between E_A and ln k_0 is clearly visible. With the average value of all ln k_0-values of 25.48 a single-parameter optimization is possible. The corresponding results are given in the last column. Actually the standard deviation of E_A values (7%) is somewhat higher than that of the Table 2 (6%).

Nevertheless the result of this evaluation may be interpreted as an encouragement for further kinetic applications, although the authors will not comment the difference of the E_A values in Tables 2 and 3.

Fig. 2. Three experimental curves of the first reaction step showing great differences of the temperatures at maximum conversion rates.

5.2. Step 2: CO-split off

For the next step, the removal of carbon monoxide, 39 measurements were sent in and handled in 304 single- and 48 overall-evaluations. In this case it was necessary to fit the curves by different models. The Tables 4–9 show the kinetic evaluations for inertia and air atmosphere on the basis of a n-order reaction for
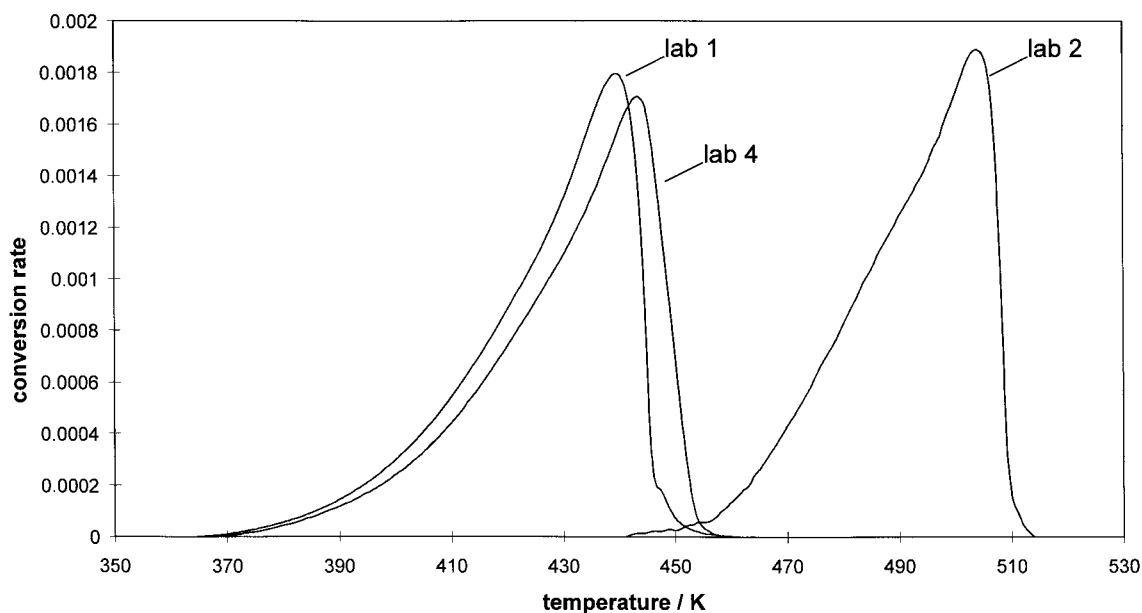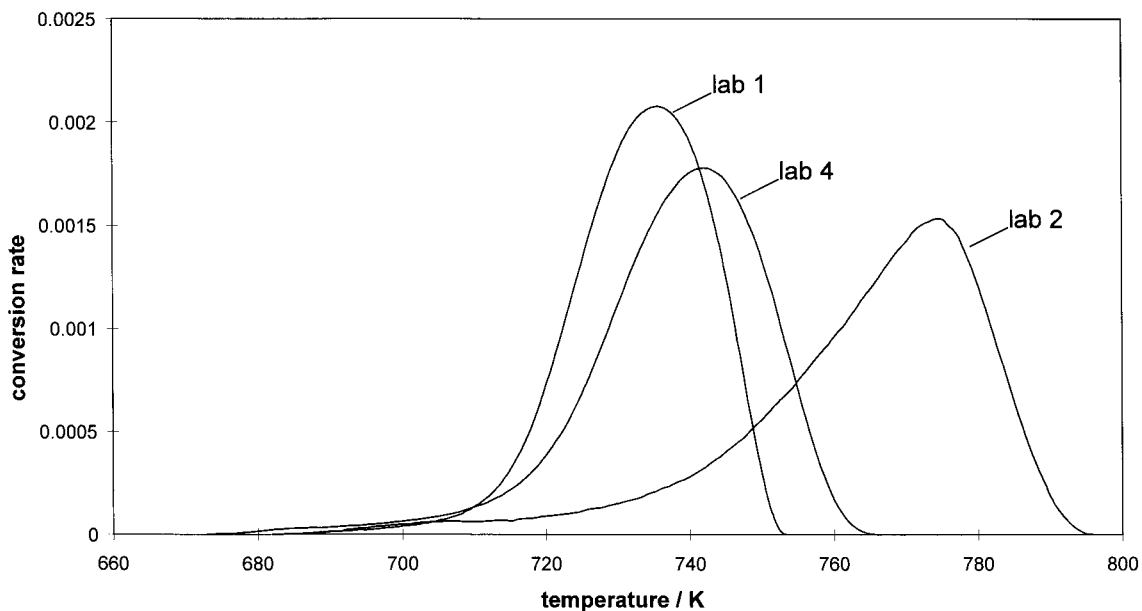

Fig. 3. Three experimental curves of the second reaction step showing great differences of the temperatures at maximum conversion rates.
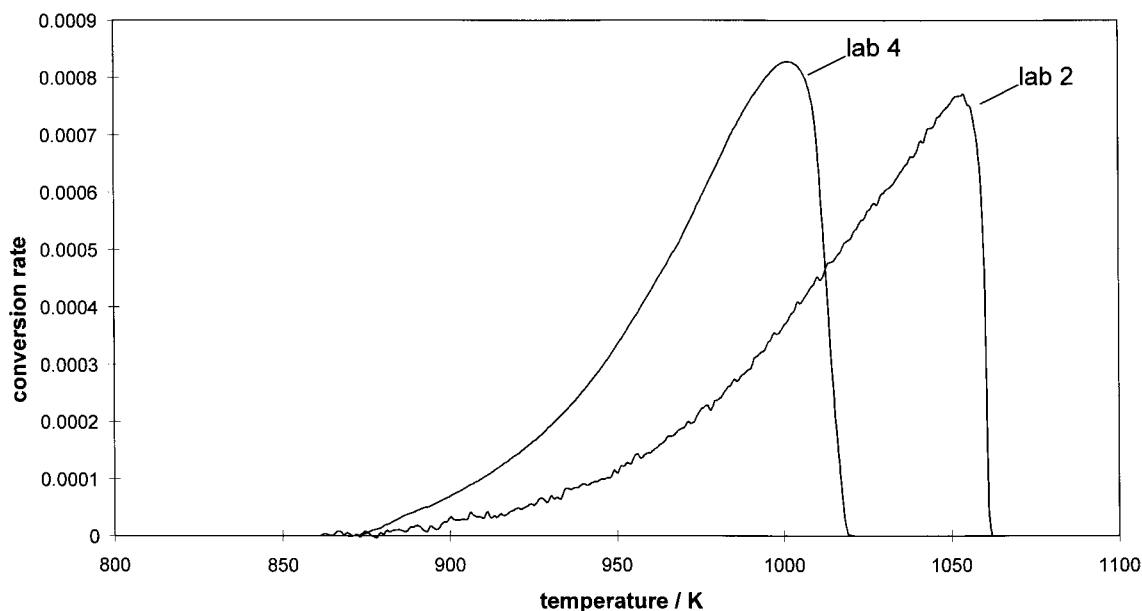
Fig. 4. Two experimental curves of the third reaction step.

$n=1/2$, 2/3 and 1. The comparison of the results has been performed in the same way as for step 1. The one-parameter optimization of the data sets obtained for inertia atmosphere lead to almost satisfactory results. The comparison of the sum of the relative sums of least squares should allow a statement about the correct order of the considered process. This leads to the close decision for a reaction order of $n=2/3$ with a sum of 2.915 in relation to, on the other hand, 2.927 for $n=1/2$. Whereas an order $n=1$ gives to the sum of

6.814. The validation of the Tables 4 and 5 does not guarantee that an order of $n=2/3$ is true without any doubt. The evaluating scientist should only include reaction orders which are supported by rational kinetics, reaction orders of other rational fractions should be neglected. It is well known that the difficulties of an exact decision are actually caused by the quality of the experimental data. At present the experimental devices do not allow higher precision and reproducibility.

The compensation plots in Figs. 7–9 demonstrate, again, the correlation of $\ln k_0$ and E_A. As described
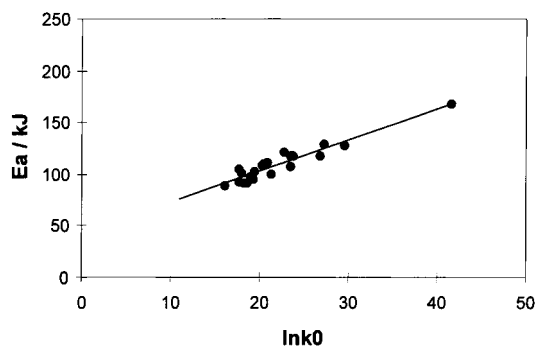
Fig. 5. The compensation plot of the results of all single evaluations of the first reaction step in inertia atmosphere (evaluated as a phase-boundary reaction R2) showing a linear correlation between these kinetic parameters.

Fig. 6. The compensation plot of the first reaction step in air.

Table 2
Results of the evaluation of the first reaction step in inertia atmosphere as a two-dimensional phase-boundary reaction R2

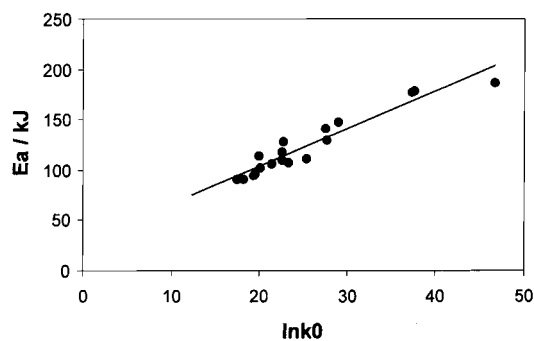| File	β (K min^{-1})	$\ln k_0$ (s^{-1})	E_A (kJ mol^{-1})	k (150°C) (s$^{-1} \times 10^4$)	SDS	Relative SDS	E_A (kJ mol^{-1}) ($\ln k_0$=22.17)
13201001	1	21.32	99.81	8.680	6.03E-07	0.136	102.6
13203001	3	18.5	90.76	6.776	4.35E-07	0.098	103.5
13210001	10	19.29	94.45	5.231	3.82E-07	0.086	105
Overall	1,3,10	16.09	82.54	6.295	1.90E-05	4.273	
23301001	1	27.27	128.9	0.854	5.26E-07	0.118	110.6
23303001	3	23.44	117.2	0.516	5.38E-07	0.121	112.4
23310001	10	22.82	121.3	0.087	3.70E-07	0.083	118.6
23301002	1	20.81	110.6	0.243	9.82E-07	0.221	115.6
23303002	3	18	101.3	0.205	1.19E-06	0.269	117.7
23310002	10	17.66	105	0.051	2.46E-07	0.055	124.4
43301001	1	16.05	87.96	1.296	1.32E-06	0.296	109.6
43303001	3	18.28	90.98	5.108	4.56E-07	0.103	104.6
43310001	10	17.66	91.87	2.134	2.08E-07	0.047	108.9
Overall	1,10	22.57	110.8	1.333	3.43E-05		
63201001	1	26.84	117.5	14.196	9.27E-07	0.209	101.9
63203001	3	19	96.6	2.124	1.75E-06	0.394	108
63210001	10	23.84	117	0.815	6.32E-07	0.142	110.6
Overall	3,10	14.73	81.69	2.057	5.73E-05		
83201001	1	19.48	102.2	0.699	1.00E-06	0.226	112
83203001	3	20.49	109.7	0.228	1.09E-06	0.245	116.2
83210001	10	20.29	108.9	0.234	4.89E-07	0.110	116.5
Overall	3,10	20.35	109.1	0.235	1.59E-06		
a3201001	1	41.63	168	21.960	4.44E-06	1.000	102.3
a3203001	3	29.5	127.4	12.171	1.68E-06	0.378	101.9
a3210001	10	23.41	107.6	7.667	9.54E-07	0.215	103.1
Overall	1,3,10	23.03	105.2	10.371	0.000177		
						Average	109.8
						Standard deviation	6.0

above it is more favorable to perform a one-parameter estimation of E_A on the basis of the average value of $\ln k_0$ to avoid any discussion about the so-called compensation effect. We come to a standard deviation of the activation energy of 2.6% each time from the average of E_A can be calculated.

Tables 7–9, characterizing the CO-split off, show strong scatter of the activation energy values within the experimental series of the same lab. Thus one should change to an one-parameter optimization. In this case, comparing the sums of the relative sum of least squares, clearly a reaction order of n=2/3 is

found. So the values of Table 8 may be taken to give the kinetic results recommend from this round robin evaluation. The standard deviation of the activation energies obtained by the one-parameter evaluation is 2.9% of the average of E_A. The respective compensation plot (Fig. 10) shows, once more, the expected correlation of E_A and $\ln k_0$.

5.3. Step 3: CO$_2$-split off

For the third step, the removal of carbon dioxide, 18 data files have been sent in and resulted in 36 single-

Table 3
Results of the evaluation of the first reaction step in air as a two-dimensional phase-boundary reaction R2

File	β (K min^{-1})	ln k_0 (s^{-1})	E_A (kJ mol^{-1})	k (150°C) (s^{-1}×10^4)	SDS	Relative SDS	E_A (kJ mol^{-1}) (ln k_0=25.48)
13101001	1	46.64	186.1	19.194	1.08E-06	0.274	114.3
13103001	3	19.4	94.02	6.598	4.21E-07	0.107	115.2
13110001	10	19.48	95.43	4.787	2.21E-07	0.056	117.5
Overall	1,3,10	17.3	86.93	6.062	1.49E-04		
23101001	1	37.56	178.6	0.018	3.76E-07	0.095	131.8
23103001	3	29.02	147.6	0.024	2.42E-07	0.061	133.3
23110001	10	22.69	128.4	0.010	2.45E-07	0.062	140.6
Overall	1,3	23.2	123.5	0.068	7.78E-05		
23101002	1	37.34	177.6	0.020	2.53E-06	0.642	131.7
23103002	3	27.59	141.3	0.035	1.44E-06	0.366	132.8
23110002	10	19.97	114.3	0.037	1.95E-07	0.049	138
Overall	1,3	23.58	124.7	0.070	7.58E-05		
33401001	1	23.35	107	8.563	1.60E-06	0.404	114.2
33403001	3	20.16	102.2	1.380	1.15E-06	0.293	121.8
33410001	10	22.53	117.5	0.191	2.33E-06	0.591	129.3
43101001	1	25.39	111.9	16.358	2.37E-07	0.060	112.2
43103001	3	18.25	90.9	5.071	2.54E-07	0.064	116.3
43110001	10	17.43	91.07	2.128	2.55E-07	0.065	121.5
53101002	1	27.74	129.6	1.120	3.10E-06	0.785	121.4
53103002	3	22.61	110.6	1.468	3.95E-06	1.000	121.3
53110002	10	21.4	105.9	1.665	2.47E-06	0.626	121.3
Overall	1,3,10	25.1	119.6	1.372	3.08E-05		
						Average	124.1
						Standard deviation	6.9

and six overall-evaluations. Obviously, many commercial DSC-devices does not support temperatures above 1000 K, so the number of the involved labs decreased for this degradation step. The evaluation of the curves of this step has been performed on the basis of a phase-boundary reaction R2. A free fit for a *n*-
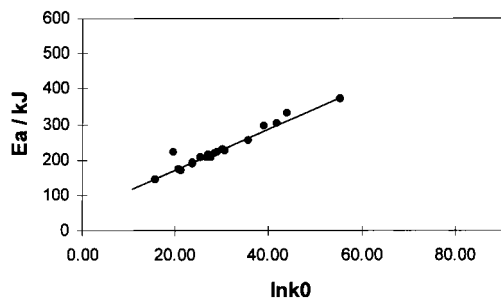

Fig. 7. The compensation plot of the second reaction step in inertia atmosphere (evaluated as a *n*-order reaction R*n* with *n*=1/2) showing a linear correlation of the kinetic parameters.
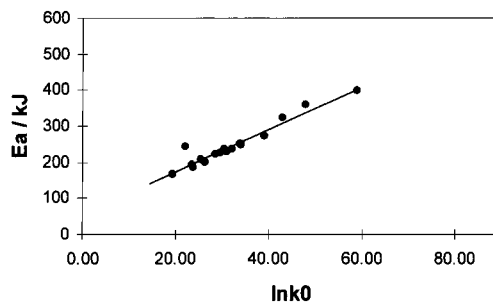

Fig. 8. The compensation plot of the second reaction step in inertia atmosphere for R*n* with *n*=2/3. This reaction order yields the best fits.

Table 4
Results of the evaluation of the second reaction step in inertia atmosphere as a *n*-order reaction R*n* with *n*=1/2

File	β (K min^{-1})	ln k_0 (s^{-1})	E_A (kJ mol^{-1})	k (450°C) (s^{-1}×10^4)	SDS	Relative SDS	E_A (kJ mol^{-1}) (ln k_0=29.83)
13201001	1	28.50	215.9	6.063	4.78E-07	0.055	223.8
13203001	3	23.75	186.2	7.329	5.61E-07	0.064	222.5
13210001	10	21.35	170.2	9.516	2.65E-07	0.030	222.5
Overall	1,3,10	30.75	228.7	6.844	6.84E-04		
23301001	1						
23303001	3	15.76	143.3	3.117	1.86E-06	0.214	231.6
23310001	10	20.66	173.8	2.623	4.06E-06	0.465	233.3
Overall	3,10	20.56	173.3	2.579	1.12E-05	1.286	
23301002	1						
23303002	3	39.18	295.9	0.439	1.11E-06	0.128	236.3
23310002	10	43.91	331.2	0.140	1.45E-06	0.166	237.8
Overall	3,10	29.82	237.2	0.657	7.84E-05		
43301001	1	19.64	220.9	0.000	9.22E-07	0.106	300.3
43303001	3	28.98	219.4	5.474	2.42E-06	0.277	224.7
43310001	10	30.32	227.6	5.346	1.96E-06	0.225	224.6
Overall	3,10	30.22	227	5.345	4.70E-06		
63201001	1	55.26	370.1	18.466	1.55E-06	0.178	224.9
63203001	3	26.76	206.6	4.998	1.87E-07	0.021	225.2
63210001	10	41.94	301.5	2.733	2.91E-06	0.333	224.9
Overall	3,10	32.11	239.2	4.651	2.10E-05		
83201001	1	27.12	213.9	2.127	1.55E-06	0.177	230.2
83203001	3	25.61	204.6	2.207	5.81E-07	0.067	230.9
83210001	10	23.9	189.7	4.758	7.27E-07	0.083	233.2
Overall	1,3,10	23.44	191.6	2.190	1.14E-05		
a3201001	1	35.71	253.3	16.312	2.49E-07	0.029	219.4
a3203001	3	30.73	225	12.413	1.50E-06	0.172	219.7
a3210001	10	27.62	206.4	12.210	1.17E-06	0.134	220
Overall	3,10	29	214.8	12.003	9.89E-06		
					Sum of relative SDS	2.927	Average	230.8
							Standard deviation	7.7

order reaction (F*n*) was as unsatisfactory as a diffusion controlled reaction (D*n*). However, the description of the process R2 is mathematical congruent to a *n*-order reaction with *n*=1/2. A decisive discussion of these two models is, however, not possible on the basis of our experimental material. Table 10 shows the results of two series of measurements from the same laboratory. It demonstrates the difficulties to define corresponding activation parameters. The differences

between the estimated activation parameters can reach 50% and more, although the linearity of the compensation plot in Fig. 11 is completely fulfilled. This is an indication for the known sensitivity of the optimization procedure on small experimental uncertainties and changes of the process conditions. This is also indicated for the single-parameter optimization of E_A with fixed ln k_0 average of 17.97. This way a standard deviation of 2.4% of the average of E_A can be

Table 5
Results of the evaluation of the second reaction step in inertia atmosphere as a n-order reaction Rn with $n=2/3$

File	β (K min^{-1})	ln k_0 (s^{-1})	E_A (kJ mol^{-1})	k (450°C) (s$^{-1} \times 10^4$)	SDS	Relative SDS	E_A (kJ mol^{-1}) (ln k_0=23.03)
13201001	1	32.11	236.7	7.048	1.56E-07	0.018	183.3
13203001	3	26.24	200.5	8.195	2.29E-07	0.026	181.4
13210001	10	23.7	184.2	9.723	1.43E-07	0.016	180
Overall	1,3,10	31.8	234.5	7.454	7.45E-04		
23301001	1						
23303001	3	19.46	166	2.891	2.26E-06	0.259	188.3
23310001	10	23.56	192.1	2.272	6.90E-06	0.792	188.6
Overall	3,10	21.96	181.7	2.586	1.14E-05		
23301002	1						
23303002	3	43.02	320	0.371	7.75E-07	0.089	192.5
23310002	10	47.77	356.4	0.101	8.33E-07	0.096	192.4
Overall	3,10	31.59	248.2	0.619	1.02E-04		
43301001	1	22.24	240.4	0.000	1.45E-06	0.166	246.6
43303001	3	34.01	249.8	5.334	1.21E-06	0.139	182.4
43310001	10	33.68	248.2	5.003	5.52E-07	0.063	181.5
Overall	3,10	32.51	240.7	5.406	3.10E-06		
63201001	1	58.99	397.8	7.682	7.48E-07	0.086	184.3
63203001	3	29.51	222.7	5.372	8.16E-07	0.094	183.6
63210001	10	25.54	205	1.925	9.84E-07	0.113	181.6
83201001	1	30.44	233.4	2.297	9.12E-07	0.105	188.7
83203001	3	28.39	221.4	2.176	1.23E-07	0.014	188.2
83210001	10	25.55	205	1.945	9.84E-07	0.113	188.8
Overall	1,3,10	24.4	197	2.329	1.99E-05		
a3201001	1	39.17	272.8	20.261	7.98E-07	0.091	179.9
a3203001	3	34.04	244.2	13.949	3.16E-06	0.362	178.9
a3210001	10	31.1	227.2	12.464	2.38E-06	0.273	177.6
Overall	3,10	30.21	221.4	13.430	2.10E-05		
					Sum of relative SDS	2.915	Average	187.8
							Standard deviation	7.9

obtained. This underlines the fact, that data obtained in the same lab and possibly by the same operator are characterized by a higher degree of compatibility. This is even true for the heating rate of 1 K min^{-1} which shows scatter of 2–3% for the curve maximum.

Starting from the distribution of incidence of each pair of parameters from Fig. 11, mean values of ln k_0=19.7 and E_A=231.8 kJ mol^{-1} appear. This is in satisfactory agreement with the discussion of mean values from the last column of Table 10.

Table 11 represents the results of the CO_2-split off in air atmosphere. A notable difference to the values of Table 10 is the lower scatter of the single evaluation results, although the k-values of lab 4 for 700°C differ significantly from the rate constants of the other labs. In the compensation plot of Fig. 12 the frequencies can be stated such, as to give a fixed ln k_0 17.8 and E_A by 215.4 kJ mol^{-1}. The last column of Table 11 shows the results of the single-parameter optimization of E_A using the average value of ln k_0=19.66. Now activa-

Table 6
Results of the evaluation of the second reaction step in inertia atmosphere as a n-order reaction Rn with $n=1$

File	β (K min^{-1})	ln k_0 (s^{-1})	E_A (kJ mol^{-1})	k (450°C) (s$^{-1} \times 10^4$)	SDS	Relative SDS	E_A (kJ mol^{-1}) (ln k_0=38.47)
13201001	1	39.59	273.7	26.549	1.63E-06	0.187	273.14
13203001	3	31.26	231.7	6.920	1.18E-06	0.135	272.8
13210001	10	28.72	214	10.363	1.42E-06	0.163	274.3
Overall	1,3,10	34.54	249.3	9.847	9.85E-04		
23301001	1						
23303001	3	15.05	143.2	1.558	1.86E-06	0.214	283.1
23310001	10	19.97	173.9	1.294	4.06E-06	0.465	287.8
Overall	3,10	25.21	201.3	2.561	3.26E-05		
23301002	1						
23303002	3	51.2	371.3	0.261	1.89E-06	0.216	289.9
23310002	10	43.12	330.6	0.070	1.45E-06	0.166	293.5
Overall	3,10	29.13	237.2	0.329	7.84E-05		
43301001	1	27.46	279.8	0.000	4.48E-06	0.514	365.7
43303001	3	44.45	312.7	5.220	2.42E-06	0.277	276.1
43310001	10	40.74	291.4	4.416	1.02E-06	0.117	277.1
Overall	3,10	37.69	271.7	5.538	1.87E-05		
63201001	1	69.24	457.9	9.906	1.75E-06	0.201	274.8
63203001	3	35.35	257.1	6.049	3.94E-06	0.452	276.1
63210001	10	56.09	389.4	1.709	5.16E-07	0.059	277.9
Overall	3,10	36.71	266.4	5.019	6.47E-05		
83201001	1	37.30	273.8	2.644	1.62E-06	0.186	280.8
83203001	3	34.22	256.6	2.123	1.53E-06	0.175	283
83210001	10	30.8	237.8	1.584	3.45E-06	0.395	287.5
Overall	1,3,10	26.6	209.6	2.586	5.77E-05		
a3201001	1	46.66	315.2	31.400	3.70E-06	0.424	267.8
a3203001	3	41.03	284.7	17.984	8.25E-06	0.946	269.4
a3210001	10	38.59	272	12.958	6.89E-06	0.790	271.2
Overall	3,10	34.45	246	15.581	2.91E-05		
					Sum of relative SDS	6.084	Average	283.3
							Standard deviation	7.5

tion energies are relatively close to each other. Resulting in a standard deviation of the satisfactory value of 2.9% of the average of E_A=231.7 kJ mol^{-1}.

Surprisingly the results from the round robin are very satisfactory. Certainly this will encourage future scientists to investigate the kinetics of similar reactions in solid state by using instruments of modern thermal analysis. The third step, the decomposition of calciumoxalate monohydrate, appears as the step with the least outer disorder. While for the first two steps critical doubts must be allowed about the validity of the determined kinetic parameters. The last step, the classic calcium carbonate decomposition with its, in the literature given [5], apparently wide distributed activation parameters, unquestionable serves as a proof for the applicability of non-linear kinetic procedures to qualitative high valued DSC-data files.

Table 7
Results of the evaluation of the second reaction step in air as a n-order reaction Rn with $n=1/2$

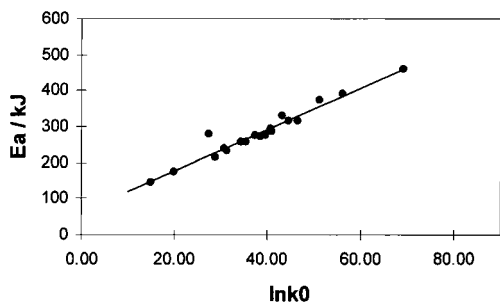| File	β (K min^{-1})	ln k_0 (s^{-1})	E_A (kJ mol^{-1})	k (450°C) (s$^{-1} \times 10^4$)	SDS	Relative SDS	E_A (kJ mol^{-1}) (ln k_0=41.06)
13101001	1	34.24	247.6	9.679	3.57E-06	0.407	287.5
13103001	3	68.59	454.3	9.411	7.86E-06	0.895	288.5
13110001	10	56.33	385.1	4.442	3.71E-06	0.423	290.4
23101001	1	34.92	262.4	1.630	2.93E-06	0.333	299.7
23103001	3	35.66	267.3	1.512	2.61E-06	0.297	300.9
23110001	10	46.18	338.18	0.425	2.99E-06	0.341	305.5
Overall	1,3	34.34	259	1.606	6.22E-06		
23101002	1	37.04	275.5	1.537	1.94E-06	0.221	300.1
23103002	3	38.31	284.8	1.165	7.55E-07	0.086	302.1
23110002	10	46.89	343.4	0.363	1.68E-06	0.191	305.5
Overall	1,3	33.05	251.6	1.514	1.53E-05		
33401001	1	34.87	258.5	2.966	2.77E-06	0.315	295.7
33403001	3	27.59	225.7	0.478	1.66E-06	0.189	312.8
33410001	10	27.83	224.6	0.730	1.01E-06	0.115	312.1
Overall	3,10	34.88	272.2	0.307	4.05E-05		
43101001	1	45.86	317.7	9.309	1.67E-06	0.190	289.4
43103001	3	53.29	365.1	5.915	2.93E-06	0.334	291
43110001	10	55.36	381.6	3.014	2.70E-06	0.308	292.4
Overall	1,3,10	35.92	259.9	6.714	8.45E-05		
53101002	1	33.97	245.2	11.013	3.71E-06	0.422	286.6
53103002	3	30.43	224.9	9.350	9.32E-07	0.106	288.7
53110002	10	31.76	231.9	11.035	2.48E-07	0.028	289.2
Overall	1,3,10	32.73	238.2	10.209	2.60E-05		
					Sum of relative SDS	5.202	Average	296.6
							Standard deviation	2.9

Fig. 9. The compensation plot of the second reaction step in inertia atmosphere for Rn with $n=1$. This reaction order does not describe experimental curves well.
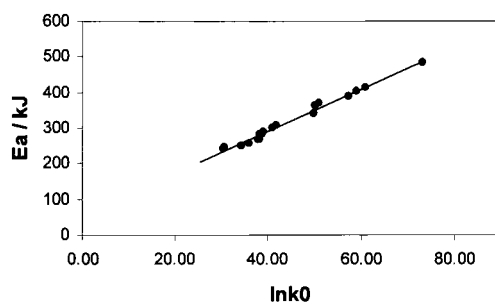
Fig. 10. The compensation plot of the second reaction step in air (for Rn with $n=2/3$) showing a linear correlation of the obtained kinetic parameters.

Table 8
Results of the evaluation of the second reaction step in air as a n-order reaction Rn with $n = 2/3$

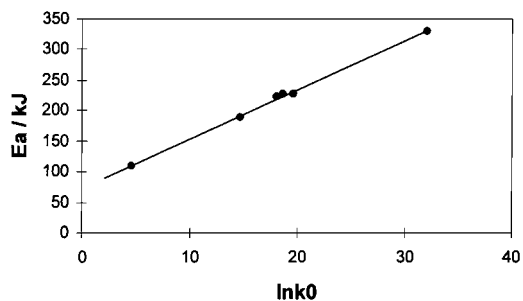| File	β (K min^{-1})	ln k_0 (s^{-1})	E_A (kJ mol^{-1})	k (450°C) (s^{-1}×10^4)	SDS	Relative SDS	E_A (kJ mol^{-1}) (ln k_0=44.88)
13101001	1	37.89	268.5	11.517	1.85E-06	0.211	309.3
13103001	3	73.1	481.6	9.129	4.87E-06	0.555	311
13110001	10	60.94	413.3	4.100	1.87E-06	0.213	313.6
23101001	1	38.33	282.6	1.714	1.22E-06	0.139	322.4
23103001	3	39.14	288.5	1.444	1.07E-06	0.122	324.3
23110001	10	50.08	363.7	0.301	2.27E-06	0.258	329.8
Overall	1,3	36.24	270.2	1.667	6.44E-06		
23101002	1	40.97	299	1.570	7.06E-07	0.080	322.8
23103002	3	41.76	306	1.080	7.42E-07	0.084	325.6
23110002	10	50.82	368.5	0.284	2.15E-06	0.245	329.8
Overall	1,3	35.14	264	1.556	2.34E-05		
33401001	1	38.88	282.1	3.228	1.31E-06	0.150	318.2
33403001	3	30.63	244.8	0.417	4.17E-07	0.048	337.1
33410001	10	30.57	242.1	0.615	1.50E-06	0.170	336.9
Overall	3,10	36.46	238.9	378.754	2.72E-05		
43101001	1	49.87	340.9	10.831	8.95E-07	0.102	311.5
43103001	3	57.25	388.6	6.228	1.56E-06	0.178	313.6
43110001	10	59.01	403.9	2.842	1.77E-06	0.202	315.7
Overall	1,3,10	37.08	266.5	7.146	1.12E-04		
53101002	1	38.12	268.8	13.790	1.09E-06	0.124	308.4
53103002	3	34.44	248.3	10.522	4.67E-07	0.053	311.1
53110002	10	35.99	257.3	11.096	1.45E-06	0.165	312.2
Overall	1,3,10	34.05	245.4	11.540	2.70E-05		
					Sum of relative SDS	3.098	Average	319.6
							Standard deviation	2.9

Fig. 11. The compensation plot of the third reaction step in inertia atmosphere (evaluated as a phase-boundary reaction R2) showing a linear correlation of the kinetic parameters.
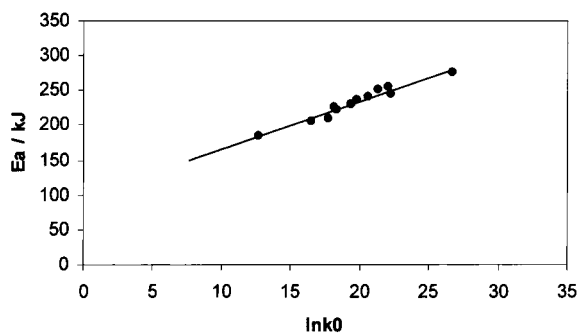

Fig. 12. Compensation plot of the third reaction step in air.

Table 9
Results of the evaluation of the second reaction step in air as a *n*-order reaction R*n* with *n*=1

File	β (K min^{-1})	ln k_0 (s^{-1})	E_A (kJ mol^{-1})	k (450°C) (s$^{-1}\times10^4$)	SDS	Relative SDS	E_A (kJ mol^{-1}) (ln k_0=53.40)
13101001	1	45.81	313.8	16.939	2.62E-07	0.030	358.2
13103001	3	84.66	549.9	11.155	1.36E-06	0.155	361.3
13110001	10	70.97	474.7	3.418	2.54E-07	0.029	365.4
23101001	1	45.70	326.4	1.866	7.73E-07	0.088	373.4
23103001	3	46.44	333	1.305	7.60E-07	0.087	376.5
23110001	10	58.67	418.6	0.175	3.06E-06	0.348	384.2
Overall	1,3	40.7	296.6	1.787	2.02E-05		
23101002	1	49.33	349	1.641	2.29E-07	0.026	373.8
23103002	3	49.3	352.2	0.935	3.18E-06	0.363	378
23110002	10	59.42	423.4	0.167	4.92E-06	0.560	384.2
Overall	1,3	39.78	291.7	1.608	4.93E-05		
33401001	1	46.90	329.3	3.826	3.62E-07	0.041	368.4
33403001	3	37.18	286.1	0.303	9.28E-07	0.106	391.3
33410001	10	36.51	280.1	0.421	4.36E-06	0.496	392.3
Overall	3,10	40.22	305.4	0.256	1.34E-05		
43101001	1	59.00	393.8	15.092	1.09E-06	0.125	360.7
43103001	3	67.08	447.3	6.660	2.35E-07	0.027	364.3
43110001	10	68.54	462.4	2.327	1.78E-06	0.203	367.8
Overall	1,3,10	39.59	280.8	8.151	1.85E-04		
53101002	1	47.36	321.6	21.810	9.91E-07	0.113	356.9
53103002	3	43.18	299.5	13.171	4.91E-06	0.559	361.1
53110002	10	45.21	312.8	10.979	8.78E-06	1.000	363.5
Overall	1,3,10	37.29	263.5	14.519	9.47E-05		
					Sum of relative SDS	4.355	Average	371.2
							Standard deviation	3.0

6. Conclusion

The sum of kinetic evaluations of DSC-data sets for the three-step reaction of calciumoxalate monohydrate may serve as a source for the following cognitions:

1. Kinetic evaluations of DSC-data can be recommended if the experimental execution of the measurements is well founded and the chemical and physical processes are realized from literature or from the experience of the operator.
2. Experimental conditions have to be chosen so as to guarantee a reliable good signal noise ratio between the error of measurement and the signal.

If necessary heating rate and gas flow have to be optimized due to the reaction in question.

3. The software used for data processing must not influence the kinetic information contained in the measured data sets. The use of such non-linear evaluation procedures frequently leads to a success if the variation of the applied basic models corresponds to all chemical knowledge about the process in question.
4. The change of the experimental conditions promotes the success of the determination of reliable kinetic parameters and supports the chosen reaction model. Every scientist who is active in basic research will always use different operating conditions.

Table 10
Results of the evaluation of the third reaction step in inertia atmosphere as a two-dimensional phase-boundary reaction R2

File	β (K min^{-1})	ln k_0 (s^{-1})	E_A (kJ mol^{-1})	k (700°C) (s$^{-1}\times10^4$)	SDS	Relative SDS	E_A (kJ mol^{-1}) (ln k_0=17.97)
23301001	1	4.693	108.1	1.721	5.26E-07	0.431	207.7
23303001	3	14.72	186.8	2.324	8.35E-07	0.684	213.1
23310001	10	19.59	226.6	2.213	1.07E-06	0.872	212.8
Overall		18.01	213.3	2.359	7.10E-06		
23301002	1	32.08	328.1	2.096	9.82E-07	0.804	216.2
23303002	3	18.65	225.7	0.966	1.14E-06	0.937	220.1
23310002	10	18.1	222.4	0.838	1.22E-06	1.000	221.3
Overall		16.36	207	0.987	8.20E-06		
						Average	215.2
						Standard deviation	2.4

Table 11
Results of the evaluation of the third reaction step in air as a two-dimensional phase-boundary reaction R2

File	β (K min^{-1})	ln k_0 (s^{-1})	E_A (kJ mol^{-1})	k (700°C) (s$^{-1}\times10^4$)	SDS	Relative SDS	E_A (kJ mol^{-1}) (ln k_0=19.66)
23101001	1	22.1	254.3	0.888	5.17E-07	0.456	230.2
23103001	3	20.66	241.1	1.075	2.42E-07	0.214	232.9
23110001	10	21.39	249.8	0.761	7.87E-07	0.693	234.8
Overall	1,3,10	15.29	196.5	1.239	5.17E-05		
23101002	1	19.37	230.5	1.097	9.98E-07	0.879	232.8
23103002	3	18.36	222.6	1.061	8.74E-07	0.770	233.3
23110002	10	19.83	237	0.778	8.90E-07	0.784	235.6
Overall	1,3,10	16.58	208.2	1.060	1.55E-05		
33401001	1	16.48	204.6	1.497	9.52E-07	0.838	229.8
33403001	3	12.69	184.4	0.411	8.15E-07	0.718	244.6
33410001	10	18.2	225.8	0.609	1.14E-06	1.000	238.7
Overall	1,10	10.38	156.8	1.235	6.01E-05		
43101001	1	26.79	275	7.483	7.61E-07	0.671	220.7
43103001	3	22.28	244	3.796	3.13E-07	0.276	223.1
43110001	10	17.78	208.2	3.520	7.94E-07	0.699	223.7
Overall	1,3,10	16.29	195.5	3.812	7.37E-05		
						Average	231.7
						Standard deviation	2.9

5. All together this round robin experiment has been successful, it includes the invitation to a deeper reflection of every such experiment.

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- D. Schultze, BAM Berlin.
- A.A. Kossoy u. A.S. Benin, GIPH St. Petersburg.
- G.K. Leitner, IKTS Dresden.
- M. Epple, Universität Hamburg.
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- Perkin-Elmer, Bodenseewerk, Goth und Wasmer.

- Applikationslabor Netzsch, Post und Henderson.
- H.J. Flammersheim und N. Eckardt, Universität Jena.
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Acknowledgements

References

[1] H.L. Anderson, A. Kemmler, G.W. Höhne, K. Heldt, R. Strey, Round robin test on the kinetic evaluation of a complex solid state reaction from 13 European laboratories. Part 1. Kinetic TG-analysis, Thermochim. Acta, this issue.

[2] H.L. Anderson, A. Kemmler, R. Strey, J. Thermal Anal. 47 (1996) 543–557.

[3] N. Eisenreich, Direct least square fit of chemical reaction curves and its relation to the kinetic compensation effect, J. Thermal Anal. 19 (1980) 289–296.

[4] H.L. Anderson, R. Strey, A. Kemmler, D. Haberland, J. Thermal Anal. 49 (1997).

[5] A. Reller, M. Maciejewski, Thermochim. Acta 110 (1987) 145.