

Round robin test on the kinetic evaluation of a complex solid state reaction from 13 European laboratories. Part 1. Kinetic TG-analysis

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Abstract

In 1994 the decomposition of calciumoxalate monohydrate as a three-step reaction has been investigated by 13 labs using the TG-method. The authors working group performed objective kinetic evaluations of 144 TG data sets obtained from the same charge of substance in different laboratories. A non-linear optimization procedure was applied for different reaction models to perform single and overall optimizations. 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 CO₂-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 TG. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Round robin test; Kinetic TG-analysis; Complex solid state reaction

1. Introduction

The round robin test (RRT) has been initiated by the kinetic working group of the German Society of Thermal Analysis (GEFTA). During the last 20 years some authors critically dealt with kinetic analysis of TA experimental results of solid state materials. Nevertheless, the great number of publications on this topic shows that there is an optimistic attitude towards this problem too. The application of kinetic rate laws for evaluation of TA experiments is in several cases doubtful but many colleagues perform, however, such analyses in a careful way. This fact motivated us to try to realize conditions which allow to get satisfactory results from the analysis, on the basis of exact experi-

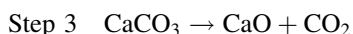
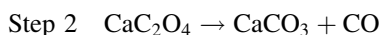
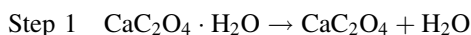
mental work in every participating laboratory. An essential characteristic of this RRT was that all laboratories used the same material (calcium oxalate monohydrate from one charge) for their measurements and the same experimental conditions. Another characteristic was that all kinetic evaluations were done by one group only (the Greifswald group) using a modern chemical kinetics non-linear evaluation computer program (software package TA-kin [1]).

The measurements were performed from September 1994 to March 1995. The intention of this extensive project with 144 experimental TG data sets, leading to about 400 kinetic evaluations, was not to support any prejudice but to explain the obtained results on the basis of a critical optimism. Measurements, which thus did not fulfill the high demands of quality, have been cancelled. For this reason, strictly,

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anonymity due to the respective lab had to be ensured. We would like to emphasize that it was by no means the aim of the RRT, or of the workgroup of the GEFTA, to judge the quality of the participating labs or the quality of the commercial equipment in question.

2. Experimental



The above-mentioned three-step reaction (see steps 1–3) has been chosen because of

- the well-known chemistry of each single step,
- the possibility to separate the single steps easily from the data files,
- processes depending on the lattice are less complicated than those of many other solid state reactions.

The last step, namely the decomposition of CaCO_3 , has been investigated frequently since thermal analysis has been applied. However, the comparison of these kinetic evaluations is problematic because of the use of simple instruments, developed during the last decades, and the choice of different substances with different structure, using different sample masses at different experimental conditions [2].

All laboratories have used the following experimental conditions:

- Sample mass: 10 mg
- Heating rates: 1, 3 and 10 K min⁻¹, respectively
- Atmosphere: air or oxygen and inert gas (N₂, He, Ar), respectively

3. Remarks on kinetic evaluations in thermal analysis

A kinetic model of reactions in solids is frequently based on the first-order ordinary differential equation ODE-approach (1), which follows from homogeneous chemical kinetics,

$$\frac{d\alpha}{dt} = k(T)f(\alpha), \quad (1)$$

where α is the dimensionless degree of reaction of the generalized process, $k(T)$ the temperature dependent rate constant according to Arrhenius and $f(\alpha)$ a conversion function. Several functions have been recommended for different solid state reactions, see Table 1. Often they result from simplified mathematical expressions.

3.1. Linearized kinetic evaluation as a historical method

Because of the mathematical structure of the models based on Eq. (1) a direct regression according to Gauss for the adjustment of model parameters to experimental data sets is not possible without further efforts. Transformations and approximation formulas yield functions with structure shown in the following equation:

$$y(x_1, x_2, \dots, x_n) = a_0 + \sum_{j=1}^n a_j x_j. \quad (2)$$

The coefficient vector \mathbf{a} contains the searched model parameters, which can be obtained after transformation of measured data and linear ($n=1$) or multiple linear ($n>1$) regression.

Looking at the experimental conditions an isothermal experiment represents the simplest case for kinetic evaluations, because Eq. (1) can be integrated analytically:

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = k \int_{t_0}^t dt. \quad (3)$$

However, the difficulties in performing exact isothermal experiments with solid state reactions are well known. In temperature-programmed thermal analysis (e.g. with linear temperature program $T(t)=T_0+\beta t$) normally the experimental conditions can be kept constant easier.

$$\frac{d\alpha}{dT} = \frac{k_0}{\beta} \exp\left(-\frac{E_A}{RT}\right) f(\alpha). \quad (4)$$

As an integrative evaluation with direct application of Eq. (3) is not allowed for non-isothermal experiments, some different procedures have been developed. The logarithm of Eq. (4) provides a relationship that can be used to determine the activation parameters

Table 1
Frequently used kinetic models for solid state reactions

Type of kinetics	Based on	Symbol	$f(\alpha)$
Formal	n th Order kinetics	F_n	$(1-\alpha)^n$
Diffusion	One-dimensional, parabolic law	D1	$\frac{1}{2\alpha}$
	Two-dimensional	D2	$-\ln(1-\alpha)^{-1}$
	Three-dimensional, Jander equation	D3	$\frac{3}{2} \frac{(1-\alpha)^{2/3}}{1-(1-\alpha)^{1/3}}$
	Three-dimensional, Ginstling–Brounshtein equation	D4	$\frac{3}{2} \frac{(1-\alpha)^{1/3}}{1-(1-\alpha)^{1/3}}$
	Three-dimensional, Carter equation	D5	$\frac{3}{2} \frac{1+(z-1)\alpha^{1/3}(1-\alpha)^{1/3}}{(1+(z-1)\alpha)^{1/3}-(1-\alpha)^{1/3}}$
Phase boundary reaction	Diffusion-controlled by geometry of phase boundary	R_n	$n(1-\alpha)^{(n-1)/n}$
Nucleation and nuclei's growth	Avrami–Erofeev equation	A_n	$n(1-\alpha)[-\ln(1-\alpha)]^{\frac{n-1}{n}}$
Autocatalysis	Prout–Tompkin equation	B1	$\alpha(1-\alpha)$

by multiple linear regression (MLR) using the transformations $y=\ln(d\alpha/dT)$, $x_1=1/T$ and $x_2=\ln f(\alpha)$ [3,4]. The simple linear procedures by Borhardt and Daniels [5] as well as Freeman and Carroll [6] have often been used in practical applications. The latter needs logarithmic and reciprocal manipulations and even the problematic differentiation of the transformed data. Consequently such a kinetic evaluation requires rather un-noisy (smoothed) input data, otherwise only ideal data sets will give reliable results.

Further development of kinetic evaluations from TA experiments in scanning mode is characterized by the introduction of integrative procedures, which reduce the number of necessary transformations of the measured data. Such procedures are especially useful for integrative experimental methods like TG. The main disadvantage of an integrative approach at a constant heating rate is the necessity to integrate k over T in Eq. (3).

$$g(\alpha) \equiv \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{k_0}{\beta} \int_0^T \exp\left(-\frac{E_A}{RT}\right) dt. \quad (5)$$

The integral on the right-hand side of Eq. (5) can only be solved approximately. Among the linear kinetic evaluation procedures, the integrative proce-

dures differ from one another by the quality of the approximation formulas and by the range of validity.

The exponential integral is often expanded in series, which is obtained after substitution of $u=E_A/RT$ in Eq. (5).

$$Ei(-x) = \int_{-\infty}^x \frac{e^{-u}}{u} du = -\frac{e^{-x}}{x} + \sum_{i=0}^{\infty} (-1)^i \frac{i!}{x^{i+1}}.$$

The simplest form has been given by Coats and Redfern [7]. After resubstitution they got a linear relation (6), which is only valid for large values of E_A/R .

$$\begin{aligned} \ln \frac{g(\alpha)}{T^2} &= \ln \left(\frac{k_0 R}{\beta E_A} \right) - \frac{E_A}{RT} \quad \text{with } g(\alpha) \\ &= \int_0^\alpha \frac{d\alpha}{f(\alpha)}. \end{aligned} \quad (6)$$

Nevertheless, overall evaluations with several data sets from different heating rates require more sophisticated methods of calculation. The so-called iso-conversion methods use either differential or integral procedures to evaluate a series of measurements with different heating rates $\beta_1, \beta_2, \beta_3, \dots$ which include the following steps:

1. computation of the experimental degree of reaction $\alpha(T)$ and its derivatives for the N heating rates β_j
2. choice of a certain α_j , e.g. $\alpha_j=0.3$, and collection of N pairs of values (T_j, β_j) for this degree of reaction
3. application of linear regression to Eq. (7) to obtain the activation parameters by a differential method [3]
4. repetition of the second and the third steps with various degrees of reaction α_j

$$\ln\left(\frac{d\alpha}{dt}\right)_{T_j} = -\frac{E_A}{RT_j} + \ln(k_0 f(\alpha_j)). \quad (7)$$

Several authors [8,9] proposed analogous algorithms for integrative evaluations.

3.2. Non-linear kinetic evaluations

Because of the increasing efficiency of computers as well as the power of higher programming languages more and more scientists in thermal analysis are in a position to determine kinetic parameters. The more general applicability of iterative methods makes them more advantageous for many users. One important aspect of non-linear evaluations is the direct determination of the parameters in an expected ODE-model. Mainly three advantages render them prominent against linear methods:

1. Applicability to complex ODE-models which cannot be transformed into linear equations;
2. There is no necessity to transform the measured data. The occurrence of distorted weights of the residuals, caused by the transformation of inevitable measurement errors during the minimization of the sum of deviation squares SDS, can thus be avoided.
3. There is no need of a defined temperature function. Interpolation tables (t_i, T_i) do not make trouble with a robust ODE-solver.

The more extensive computational effort connected with non-linear procedures, which is caused by the iterative SDS-minimization (for each iteration step about $n+1$ numeric integrations with n parameters), does not mean a real problem nowadays. However, difficult situations appear if unsuitable starting values have been chosen for the parameter optimization. By

Monte-Carlo procedures it is always possible to obtain reliable starting values [10].

4. Thermogravimetry of the thermal decomposition of calcium oxalate monohydrate

All data files from the different laboratories were treated in Greifswald by a special program, to convert them to a standardized format at which any manipulation of the experimental results has been avoided. The names were encoded to get anonymous data.

During the decomposition of the crystalline $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ there are three reaction steps visible at increasing temperature, corresponding to the splitting-off of H_2O , CO and CO_2 , respectively. The respective conversion intervals depend on the heating rate and on the atmosphere in question, e.g. for air the second step is coupled with an oxidation forming carbon dioxide.

Seven of the 12 participating laboratories performed defined TG measurements (2 labs only in air, 1 lab only in inert gas). The temperatures at respective maximal rate of conversion differ from each other by 20–100 K depending on the heating rate and atmosphere of the experiment. The standard deviations in Tables 2 and 3 for the first and the third steps reflect that fact, especially in inert gas. Figs. 1 and 2 show the corresponding measured curves for a heating rate of 1 K min^{-1} .

Table 2
Mean temperatures of the maximal conversion rate in inert gas

β (K min^{-1})	T ($^\circ\text{C}$)		
	Step 1	Step 2	Step 3
1.0	147±23	450±12	682±13
3.0	167±12	468±10	723±13
10.0	188.8±6.3	495.2±8.0	771±20

Table 3
Mean temperatures of the maximal conversion rate in air

β (K min^{-1})	T ($^\circ\text{C}$)		
	Step 1	Step 2	Step 3
1.0	140±19	452.2±5.7	671±37
3.0	154±23	471.7±5.0	710±40
10.0	181±17	495.2±5.4	755±38

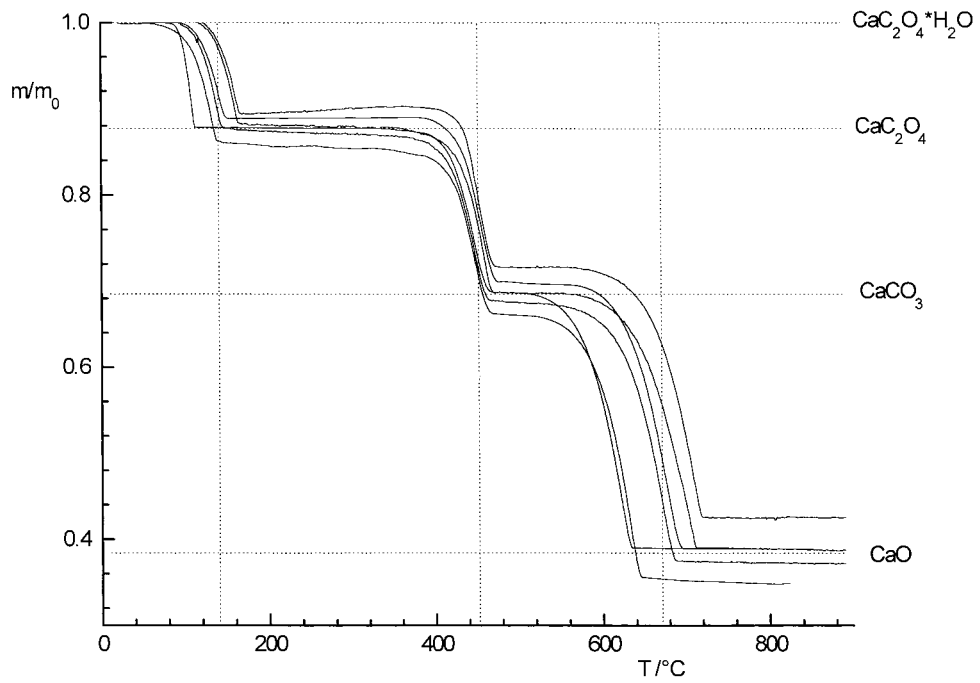


Fig. 1. Relative mass loss in inert gas, $\beta=1 \text{ K min}^{-1}$.

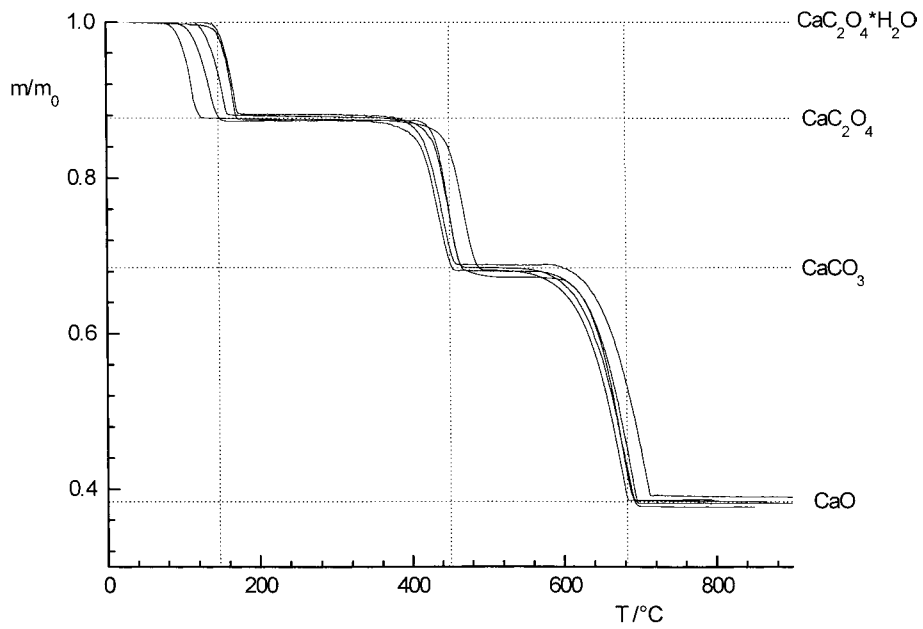


Fig. 2. Relative mass loss in air, $\beta=1 \text{ K min}^{-1}$.

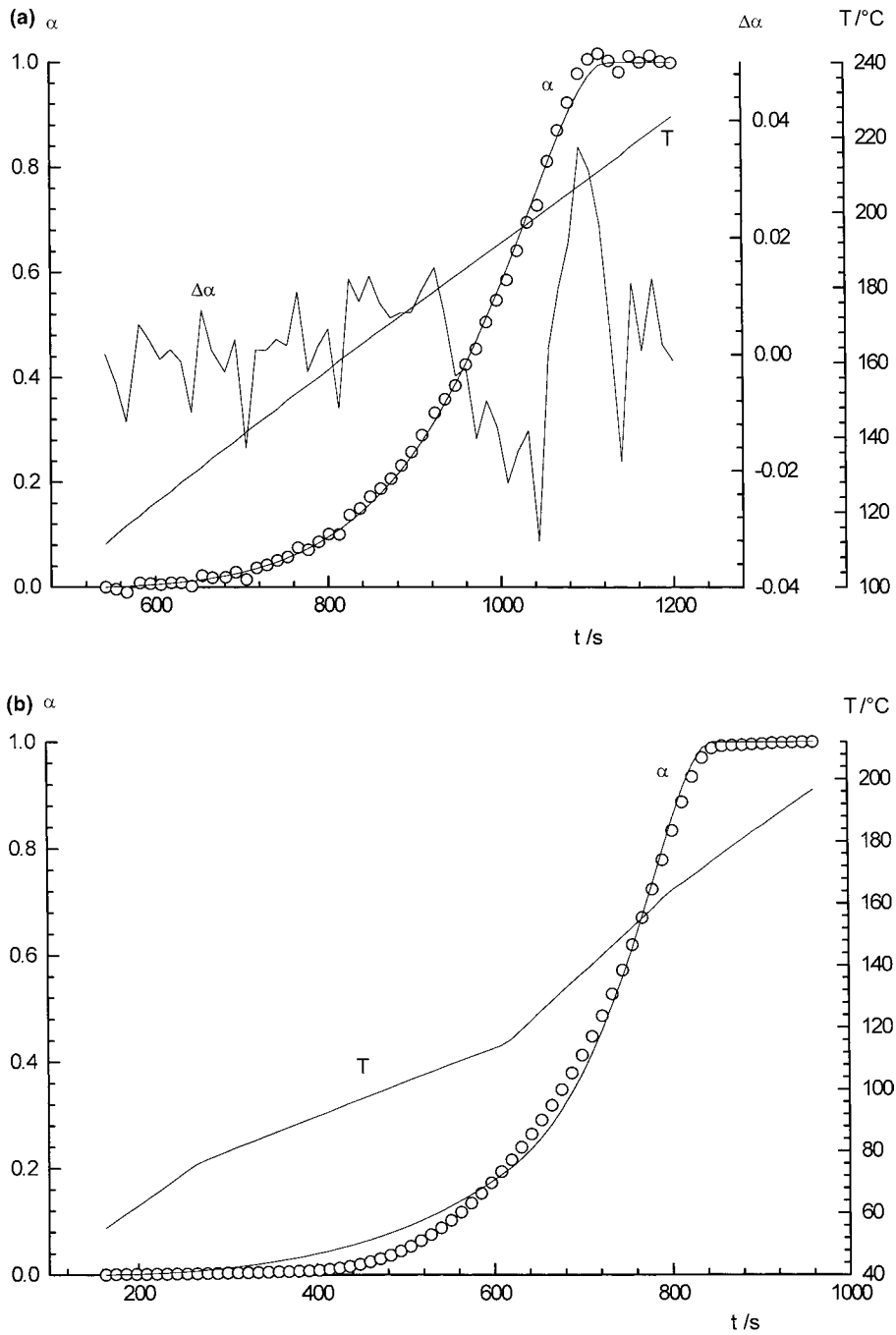


Fig. 3. (a) Evaluation of the first step in inert gas, model F1/2, $\beta=10 \text{ K min}^{-1}$, no. 92210001, (\circ) measured $\alpha(t)$, (—) simulated $\alpha(t)$, (—) calculated $\Delta\alpha(t)$, (—) measured $T(t)$; (b) evaluation of the first step in inert gas, model F1/2, $\beta=10 \text{ K min}^{-1}$, no. 12210001, (\circ) measured $\alpha(t)$, (—) simulated $\alpha(t)$, (—) measured $T(t)$; (c) overall-evaluation of the first step in inert gas, model F1/2, no. 922, (\circ), (\square), (Δ) measured $\alpha(t)$, (—) simulated $\alpha(t)$.

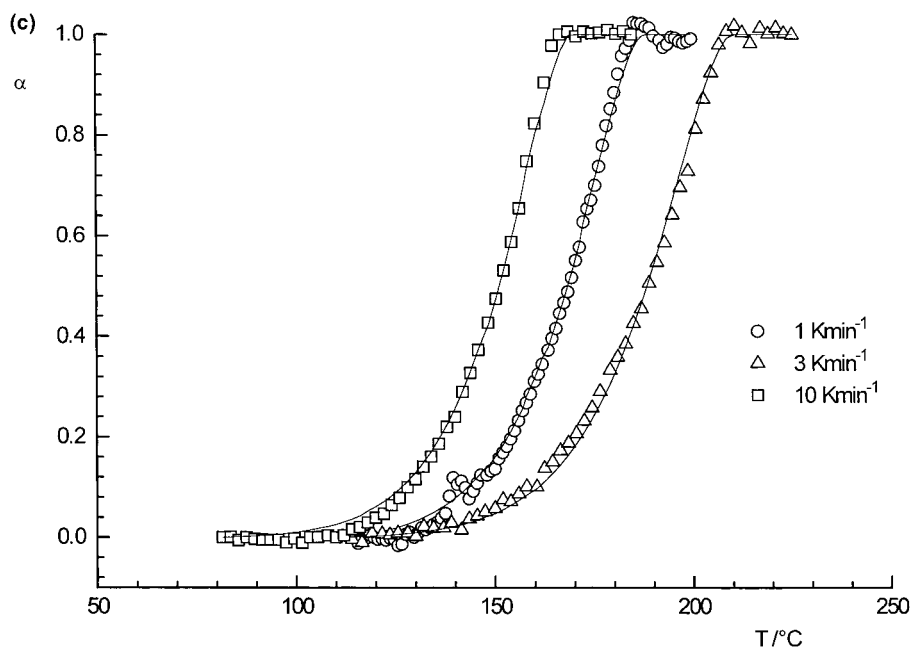


Fig. 3. (Continued)

An insufficient buoyancy correction was noticed for the data files of two laboratories. The maximal value of the relative mass increased between two reaction steps by 1% in the respective files. Beyond the third step the relative mass loss equals up to 7% in inert gas and to maximal 2% in air.

One of the participants produced data sets at 3 and 10 K min⁻¹ that showed an apparent bend within the first step which is accompanied by a systematic deviation of the local heating rate at the bend around 117°C (see Fig. 3(b)), characterized by a sudden change of the heating rate from 6 to 16 K min⁻¹ instead of constant 10 K min⁻¹ as it should be. Such experimental curves cannot be evaluated properly since a linear temperature increase is assumed.

5. The kinetic evaluation

Each reaction step was evaluated separately. First the differences between the stoichiometric and the experimental mass losses were calculated. Its relative value did not exceed 3%. Furthermore the real heating rates were derived from the recorded temperature T and time t values. With the exception of the above-

mentioned files the results were satisfactory. Nevertheless it must be stated, that different instruments from different commercial manufacturers gave deviating results.

5.1. Reaction step 1

The dehydration can be modeled with an exponent $n=1/2$ using the model F_n from Table 1 [11–13]. That is mathematically analogous to an exponent $n=2$ and the model R_n for a phase boundary reaction. Other well-founded theoretical reaction orders of $n=1/3$, $2/3$ and $3/4$ fit to the data less satisfactorily.

For the computed rate constants at a constant temperature, the results from the laboratories differ from each other up to a factor of 1000, see Tables 4 and 5. In Fig. 3(a) the evaluation of the first reaction step is shown as an example for this reaction in inert atmosphere. This data set has relative high random errors (noise), nevertheless the relative well realized constant heating rate allowed a successful kinetic evaluation and the measured α -curve is indeed optimal represented by the simulated α -curve. However, minor agreements in such plots were also found as it is shown in Fig. 3(b) for measurements from another lab.

Table 4
Evaluation of the first step in air, model F1/2

No.	β (K min ⁻¹)	ln k_0 (s ⁻¹)	E_A (kJ mol ⁻¹)	$1E4^*k$ (150°C) (s ⁻¹)	SDS	Relative SDS	E_A (kJ mol ⁻¹) (ln $k_0=22.27$)
12101001	1	27.51	110.59	198.04	5.35E-07	0.11	94.35
12103001	3	13.65	67.82	36.05	5.09E-06	1.00	95.58
12110001	10	9.15	53.13	26.04	2.55E-06	0.50	99.27
Overall		12.37	63.91	30.55			
22101001	1	39.38	166.95	3.10	7.64E-07	0.15	106.46
22103001	3	29.40	131.08	3.86	8.64E-07	0.17	105.42
22110001	10	23.18	108.61	4.57	5.67E-07	0.11	105.21
Overall		28.95	129.97	3.38			
22101002	1	37.06	159.12	2.83	2.13E-06	0.42	106.71
22103002	3	26.15	119.93	3.57	2.16E-06	0.42	105.88
22110002	10	22.31	105.94	4.07	9.41E-07	0.18	105.82
Overall		26.59	121.76	3.28			
32401001	1	24.80	111.24	10.95	7.75E-07	0.15	102.65
32403001	3	20.17	95.61	9.08	6.24E-07	0.12	102.99
32410001	10	18.08	86.46	15.12	9.25E-07	0.18	101.64
Overall		24.88	111.54	10.88			
42101001	1	19.26	88.99	23.90	2.54E-06	0.50	98.84
42103001	3	13.46	70.74	13.00	5.60E-07	0.11	101.06
42110001	10	15.38	77.45	13.15	5.44E-07	0.11	102.56
Overall		13.17	69.41	14.15			
72103001	3	17.43	83.40	18.88	7.45E-07	0.15	99.92

The resulting rate constant at 150°C is according to Table 5 about 10 times greater, i.e., depending on the instrument and on the sample holders, respectively a relative high variance of kinetic results can be expected.

For some labs, the results within the series of heating rates (1, 3, 10 K min⁻¹) are somewhat inconsistent. Related to the influence of atmosphere there are, however, only small differences between the k -values whereas the differences between different labs are much more conspicuous. As expected, the overall-evaluation for all three heating rates gives a good fit (see Fig. 3(c)), if the respective single evaluations provide rate constants of nearly the same order of magnitude. Tables 4 and 5 for the first reaction step in air or inert gas (N₂, He, Ar), respectively, express the state of the art for thermogravimetric determination of kinetics.

For most of the indicated labs in Tables 4 and 5 the kinetic descriptions of the first step led to acceptable

results compared to some skeptic presentations on this issue in the literature. Nevertheless, the difficulties resulting from the smallest heating rate of 1 K min⁻¹ are recognizable. Because of the smaller rates of conversion the uncertainties due to the stability of the signal (noise) contribute to further distortions of the measured data.

Obviously it is not possible to determine activation parameters this way that have a precision of more than three digits. Even for laboratories with an experience of many years the results scattered in the range of 5–10%. It may be interesting to learn that after a detailed discussion with the experimenters of these measurements some of them dispensed with their inclusion into the common evaluation. Especially this happened if the marginal experimental conditions did not accord with the parameters of most of the other labs.

Non-linear procedures allow overall-evaluations thus Tables 4 and 5 even contain these results. Such

Table 5
Evaluation of the first step in inert gas, model F1/2

No.	β (K min ⁻¹)	ln k_0 (s ⁻¹)	E_A (kJ mol ⁻¹)	$1E4^*k(150^\circ\text{C})$ (s ⁻¹)	SDS	Relative SDS	E_A (kJ mol ⁻¹) (ln $k_0=20.27$)
12201001	1	46.68	168.27	3163.78	1.28E-06	0.17	87.02
12203001	3	26.35	104.89	311.89	2.12E-06	0.29	85.91
12210001	10	13.59	65.12	73.42	7.33E-06	1.00	87.14
Overall		23.30	96.07	181.44			
22301001	1	21.90	98.02	25.81	1.47E-06	0.20	92.70
22303001	3	18.14	84.57	27.35	1.08E-06	0.15	91.71
22310001	10	16.92	79.61	33.25	4.55E-07	0.06	91.22
Overall		23.95	104.35	33.22			
22301002	1	23.92	109.77	6.92	1.31E-06	0.18	97.19
22303002	3	18.27	89.52	7.67	7.91E-07	0.11	96.60
22310002	10	16.54	83.62	7.23	8.75E-07	0.12	97.48
Overall		19.41	94.07	6.57			
42301001	1	22.57	100.77	23.10	8.23E-07	0.11	93.20
42303001	3	11.92	65.21	13.44	8.58E-07	0.12	93.79
42310001	10	15.34	76.94	14.52	3.24E-07	0.04	94.80
Overall		15.76	78.40	14.70			
72501001	1	15.57	75.41	28.37	1.81E-06	0.25	90.44
72503001	3	19.64	88.40	41.38	2.95E-07	0.04	90.50
72510001	10	16.91	78.76	41.84	6.59E-07	0.09	90.44
Overall		19.44	87.68	41.48			
92201001	1	21.99	103.09	6.70	2.18E-06	0.30	97.17
92203001	3	21.52	101.84	5.95	3.95E-06	0.54	97.37
92210001	10	17.10	85.77	6.92	2.34E-06	0.32	97.59
Overall		19.26	93.76	6.18			

evaluations are mathematically applicable for data sets with the same basic prerequisites, whereas difficulties arise outside the range of validity of these preconditions. Nevertheless common results were obtained within the order of magnitude of $\pm 30\%$ in Table 4 and of $\pm 12\%$ in Table 5. The summary of these results should, however, be valued in a sense, that it is not possible to agree with remarks in literature that query the seriousness of such kinetic evaluations. Such agnostic presentations cannot be accepted even for the difficult conditions of an equilibrium reaction within the first step.

By using the so-called ‘compensation’ procedure an even better conformity of the results from Tables 4 and 5 can be found. The last column of these tables contains optimized E_A -values that were computed using the average of ln k_0 -values obtained from single

evaluations. The scatter of the resulting activation energies is smaller both for the inter- and the intra-laboratory comparison. The plots of these ‘compensation’ evaluations are shown in Figs. 4 and 5. As everybody knows the ‘compensation’ effect is not a question of kinetic interpretations but a consequence of investigations on optimization of correlated parameters [1,14].

5.2. Reaction step 2

The second step of the decomposition is irreversible in contrast to the first and the third steps. Therefore the participants of the RRT expected an easier kinetic evaluation, but this is not the case in general. Nevertheless the TG investigations can be used for kinetic tasks. A special problem was the selection of a proper

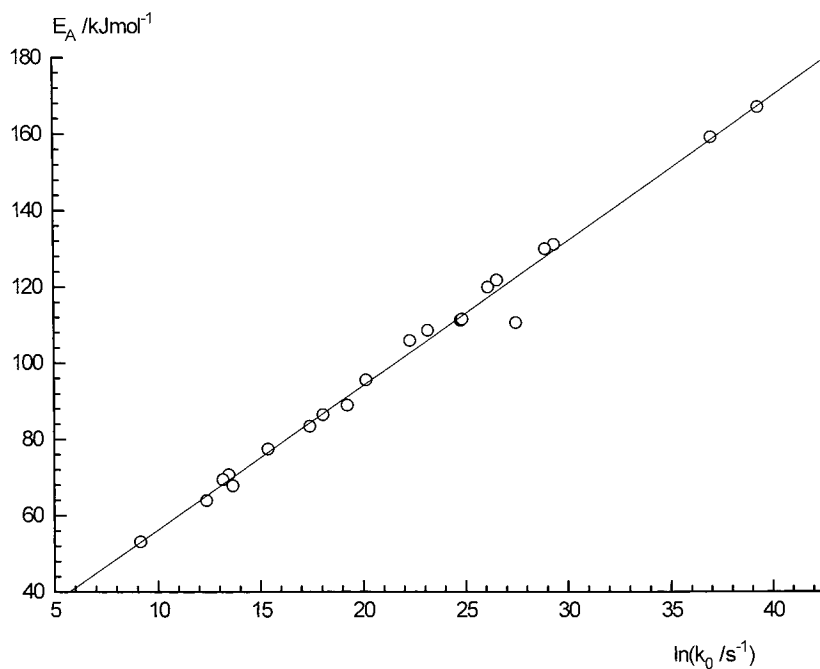


Fig. 4. Evaluation results of the first step in air, model F1/2, (○) $E_A(\ln k_0)$, (—) regression line.

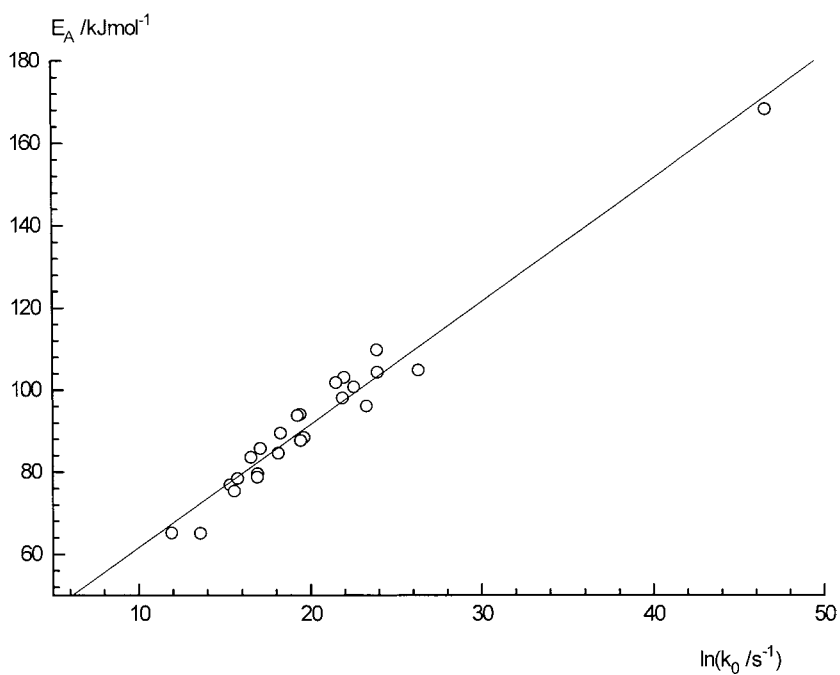


Fig. 5. Evaluation results of the first step in inert gas, model F1/2, (○) $E_A(\ln k_0)$, (—) regression line.

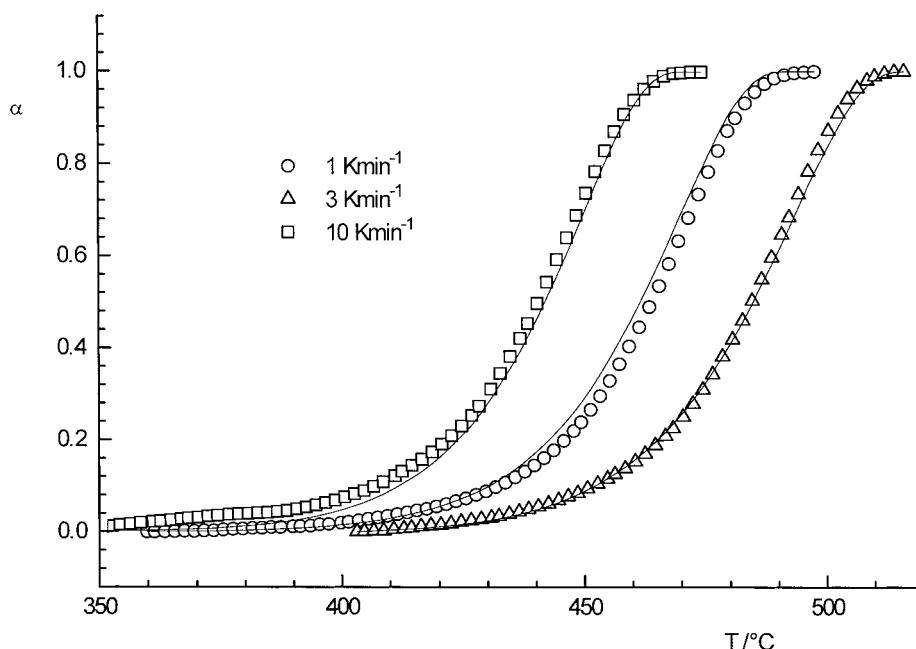


Fig. 6. Overall-evaluation of the second step in air, model F2/3, no. 221, (○), (□), (Δ) measured $\alpha(t)$, (—) simulated $\alpha(t)$.

reaction model. Obviously the chemical first-order model F1 is a bad choice.

A graphical example for an overall-evaluation is given in Fig. 6. Table 6(a)–(c) shows the results of kinetic evaluations with fixed so-called reaction orders for the CO split-off in air. Due to the activation parameters, the results from different laboratories differ from one another while the single evaluations fit relatively well to the measurements, what is confirmed by the sum of deviation squares. Because of kinetic systematics only rational values of the process order were included. As everybody knows the kinetic evaluation turns to the range of empty statements if the reaction order is treated as an open parameter to optimize. For Table 6(a)–(c) the reaction order was set to 1/2, 2/3 and 1, respectively, because for these values a model conception exists [7,11]. Even though the differences do not seem to be considerably large our critical analysis has to recommend an n -value of 2/3. This is supported by the relative SDS-values, which enable a comparison of all single evaluations in Table 6(a)–(c).

The evaluations with a fixed average value of $\ln k_0$ provide activation energies that correspond well to each other within the group of one heating rate for the

respective order. Between the different models the activation energy changes according to the graduated mean values of $\ln k_0$. This is caused by the mathematical correlation of the activation parameters as described above.

As a result, it can be stated that the RRT was successful for the second step. It should, however, not be concealed that the evaluations for a reaction order of $n=3/4$ show a mathematically better result. But we would not like to discuss this because such an order would be contradictory to our kinetic way of thinking. The influences of such a small shift of the reaction order should be treated in a special investigation.

In principle the experiments in inert gas lead us to the same statements. The corresponding results of evaluations are summarized in Table 7(a)–(c) and Fig. 7 as one graphical example. Again the relative sum of deviation squares indicates that the reaction order $n=2/3$ gives better fits than $n=1$ or $n=1/2$, respectively. A trial with $n=3/4$ was worse in this case than that with $n=1/2$.

Optimizations with fixed mean values of $\ln k_0$ resulted in activation energies, which are more close to each other than those from air measurements. This

Table 6
Evaluation of the second step in air

No.	β (K min ⁻¹)	ln k_0 (s ⁻¹)	E_A (kJ mol ⁻¹)	$1E4^*k(450^\circ\text{C})$ (s ⁻¹)	SDS	Relative SDS	E_A (kJ mol ⁻¹) (ln $k_0=35.64$)
<i>(a) Model F1/2</i>							
12101001	1	32.43	245.65	2.18	1.53E-06	0.16	266.51
12103001	3	36.52	270.16	2.22	1.57E-06	0.16	266.27
12110001	10	36.51	268.83	2.73	2.91E-06	0.30	264.94
Overall		39.95	290.97	2.16			
22101001	1	29.64	217.63	14.20	8.28E-07	0.09	253.46
22103001	3	29.11	213.82	15.81	2.14E-06	0.22	253.76
22110001	10	30.94	224.92	15.53	1.37E-06	0.14	255.18
Overall		30.66	223.14	15.79			
22101002	1	31.33	228.48	12.71	1.72E-06	0.18	254.77
22103002	3	32.82	237.56	12.38	3.81E-07	0.04	255.87
22110002	10	34.42	248.07	10.77	4.91E-07	0.05	257.09
Overall		30.61	224.43	12.08			
32401001	1	38.77	276.26	7.64	1.90E-06	0.20	259.32
32403001	3	31.61	232.75	8.28	9.01E-07	0.09	258.28
32410001	10	34.73	250.61	9.55	1.15E-06	0.12	257.76
Overall		39.51	280.25	8.26			
42101001	1	43.48	304.65	7.56	9.57E-06	1.00	259.93
42103001	3	42.34	298.37	6.85	2.12E-06	0.22	259.49
42110001	10	45.15	317.09	5.07	2.13E-06	0.22	259.62
Overall		38.70	276.68	6.66			
72103001	3	40.49	285.18	9.66	1.98E-06	0.21	257.63
<i>(b) Model F2/3 relative SDS relates to (a), no. 42101001(ln $k_0=39.04$)</i>							
12101001	1	35.61	264.34	2.35	1.10E-06	0.12	285.01
12103001	3	39.79	289.89	2.20	1.20E-06	0.13	285.21
12110001	10	40.66	294.59	2.40	2.02E-06	0.21	284.32
Overall		40.82	295.81	2.29			
22101001	1	32.60	234.11	17.60	4.49E-07	0.05	271.09
22103001	3	32.00	230.32	18.20	7.80E-07	0.08	271.85
22110001	10	33.67	241.04	16.21	9.88E-07	0.10	273.95
Overall		31.65	228.52	17.34			
22101002	1	34.30	245.16	15.49	4.96E-07	0.05	272.51
22103002	3	36.20	257.26	13.83	1.36E-07	0.01	274.16
22110002	10	37.41	265.96	10.88	8.13E-07	0.09	275.99
Overall		31.48	229.14	13.20			
32401001	1	42.44	297.33	8.99	7.96E-07	0.08	277.34
32403001	3	34.70	250.68	9.19	4.65E-07	0.05	276.61
32410001	10	38.41	272.77	9.48	2.58E-07	0.03	276.66
Overall		40.44	285.33	8.97			
42101001	1	47.09	325.48	8.71	7.39E-06	0.77	278.03
42103001	3	46.43	322.61	7.27	1.09E-06	0.11	277.99
42110001	10	48.88	339.77	4.84	1.32E-06	0.14	278.66
Overall		39.91	283.52	7.14			
72103001	3	44.40	308.18	10.55	1.40E-06	0.15	276.00

Table 6 (Continued)

No.	β (K min ⁻¹)	ln k_0 (s ⁻¹)	E_A (kJ mol ⁻¹)	$1E4^*k(450^\circ\text{C})$ (s ⁻¹)	SDS	Relative SDS	E_A (kJ mol ⁻¹) (ln $k_0=35.64$)
(c) Model F1 relative SDS relates to (a), no. 42101001 (ln $k_0=46.41$)							
12101001	1	42.85	307.04	2.70	1.42E-06	0.15	328.58
12103001	3	47.32	335.40	2.11	1.29E-06	0.13	329.80
12110001	10	47.82	338.86	1.97	1.67E-06	0.17	329.92
Overall		43.27	309.95	2.53			
22101001	1	39.08	270.38	27.61	7.70E-07	0.08	312.62
22103001	3	38.19	265.81	24.25	9.19E-07	0.10	314.42
22110001	10	39.67	276.72	17.43	3.24E-06	0.34	318.07
Overall		34.18	242.56	21.08			
22101002	1	40.95	282.60	23.55	6.69E-07	0.07	314.24
22103002	3	43.53	300.00	17.29	1.21E-06	0.13	317.19
22110002	10	43.97	305.36	10.91	4.69E-06	0.49	320.48
Overall		33.55	240.47	15.81			
32401001	1	50.47	343.63	12.57	1.06E-06	0.11	319.73
32403001	3	41.51	290.38	11.30	1.86E-06	0.19	319.74
32410001	10	46.30	320.39	9.20	1.36E-06	0.14	321.11
Overall		42.87	298.91	10.61			
42101001	1	57.47	385.93	12.13	3.82E-06	0.40	320.60
42103001	3	54.31	369.26	8.18	1.53E-07	0.02	321.53
42110001	10	56.90	388.76	4.29	8.76E-07	0.09	323.47
Overall		42.55	298.54	8.22			
72103001	3	52.26	354.37	12.54	1.78E-06	0.19	319.26

is clearly confirmed by the plots of the “compensation” evaluations. Consequently only minor systematic influences should exist, which do not seem to have a complex character.

In particular these results should motivate all laboratories with high demands on the experimental work to smooth the way for a serious kinetics. In other words, those laboratories, which do not rule over the reproducibility and the precision of the CO-split off reaction, should repeat their measurements sufficiently on a more stable basis.

It should be remarked that for some curves in inert gas a slight irregularity was observed in the region of the beginning decomposition. This may be interpreted as an additional preliminary step that comprises 3–4% of conversion. Within the framework of our investigation these appearances have not been treated especially because a model extension would be necessary in that case. The

well-founded inclusion of such an extension demands additional experimental material with sufficient precision.

5.3. Reaction step 3

The third step of the decomposition has a reversible character again, but the conditions of the experimental procedure are proper to neglect the reversibility. Table 8(a)–(c) for reactions in air summarize the results for variation of the order. The order $n=1$ was neglected because this obviously does not fit to the experimental data. Some authors reported that the third step can be fitted by orders $n=1/2$ and $n=2/3$, respectively [7,15,16]. A comparison of the relative SDS-values indicates that the order $n=1/2$ for Table 8(b) should be the best one. For $n=1/3$ and $n=2/3$ the optimized parameters resulted in more unfavorable fits to the experimental data sets. This

Table 7
Evaluation of the second step in inert gas

No.	β (K min ⁻¹)	ln k_0 (s ⁻¹)	E_A (kJ mol ⁻¹)	$1E4^*k(450^\circ\text{C})$ (s ⁻¹)	SDS	Relative SDS	E_A (kJ mol ⁻¹)
<i>(a) Model F1/2, relative SDS relates to (c), no. 22310002 (ln $k_0=31.36$)</i>							
12201001	1	27.45	207.46	8.66	1.97E-06	0.33	230.19
12203001	3	29.60	219.25	10.44	5.28E-07	0.09	229.74
12210001	10	32.06	235.59	8.02	1.16E-06	0.20	231.32
Overall		28.54	213.58	9.26			
22301001	1	26.39	201.24	8.44	2.81E-07	0.05	230.06
22303001	3	26.54	201.88	8.79	7.07E-07	0.12	230.71
22310001	10	26.47	199.76	11.71	1.00E-06	0.17	229.74
Overall		29.50	219.25	9.45			
22301002	1	31.45	233.31	6.37	4.69E-07	0.08	232.83
22303002	3	34.57	252.38	6.11	1.14E-06	0.19	232.93
22310002	10	34.12	249.64	6.13	2.02E-06	0.34	232.48
Overall		32.73	241.05	6.39			
42301001	1	29.53	222.54	5.61	8.46E-07	0.14	233.36
42303001	3	30.90	231.75	4.78	1.40E-06	0.24	234.57
42310001	10	32.59	241.92	4.79	2.97E-06	0.50	234.25
Overall		29.29	221.37	5.37			
72501001	1	26.03	199.66	7.63	1.53E-06	0.26	230.63
72503001	3	29.72	221.92	7.57	7.38E-07	0.12	231.76
72510001	10	30.74	226.94	9.05	6.30E-07	0.11	230.82
Overall		30.90	228.23	8.56			
92201001	1	42.19	297.81	6.51	2.06E-06	0.35	233.85
92203001	3	38.50	275.72	6.37	2.83E-06	0.48	232.68
92210001	10	35.70	259.58	5.68	3.97E-06	0.67	232.66
Overall		36.08	261.56	5.99			
<i>(b) Model F2/3, relative SDS relates to (c), no. 22310002 (ln $k_0=34.40$)</i>							
12201001	1	30.34	223.75	10.37	7.32E-07	0.12	247.37
12203001	3	32.33	234.99	11.65	6.48E-07	0.11	247.36
12210001	10	35.06	253.66	8.03	1.57E-06	0.26	249.59
Overall		29.48	218.70	10.16			
22301001	1	29.26	217.38	10.17	7.70E-07	0.13	247.22
22303001	3	29.41	218.51	9.74	1.32E-06	0.22	248.40
22310001	10	29.04	214.98	12.15	1.33E-06	0.22	247.89
Overall		30.49	224.62	10.41			
22301002	1	34.81	252.63	7.41	1.53E-06	0.26	250.24
22303002	3	38.15	273.58	6.44	7.46E-07	0.13	250.85
22310002	10	37.27	268.70	5.97	2.59E-06	0.44	250.88
Overall		33.70	246.37	6.90			
42301001	1	32.76	241.10	6.50	2.09E-07	0.04	250.79
42303001	3	33.40	246.46	5.07	5.15E-07	0.09	252.54
42310001	10	35.51	259.64	4.64	1.51E-06	0.25	252.75
Overall		30.21	226.46	5.80			

Table 7 (Continued)

No.	β (K min ⁻¹)	ln k_0 (s ⁻¹)	E_A (kJ mol ⁻¹)	$1E4^*k(450^\circ\text{C})$ (s ⁻¹)	SDS	Relative SDS	E_A (kJ mol ⁻¹)
72501001	1	28.78	215.14	9.12	1.80E-06	0.30	247.82
72503001	3	32.59	238.63	8.27	6.04E-07	0.10	249.52
72510001	10	33.75	245.01	9.09	5.16E-07	0.09	249.07
Overall		31.72	232.67	9.28			
92201001	1	45.94	319.52	7.46	1.05E-06	0.18	251.32
92203001	3	41.99	296.31	6.78	1.87E-06	0.32	250.53
92210001	10	38.89	278.91	5.52	2.36E-06	0.40	251.04
Overall		37.36	268.80	6.44			
(c) Model F1 (ln $k_0=41.09$)							
12201001	1	36.87	260.69	15.18	4.41E-07	0.07	285.28
12203001	3	38.69	271.90	14.56	1.97E-06	0.33	286.23
12210001	10	41.77	294.15	7.84	3.37E-06	0.57	289.92
Overall		31.67	230.70	12.31			
22301001	1	35.32	251.51	14.84	4.39E-06	0.74	285.06
22303001	3	35.47	253.75	11.91	5.47E-06	0.92	287.42
22310001	10	34.60	248.07	12.89	3.01E-06	0.51	287.95
Overall		33.05	238.78	12.76			
22301002	1	41.78	292.76	10.01	5.37E-06	0.90	288.66
22303002	3	45.87	319.41	7.11	2.00E-06	0.34	290.37
22310002	10	44.15	310.56	5.50	5.94E-06	1.00	291.49
Overall		36.03	259.54	7.99			
42301001	1	39.60	280.42	8.76	2.32E-06	0.39	289.22
42303001	3	39.73	283.87	5.61	5.21E-07	0.09	292.16
42310001	10	41.97	299.11	4.21	1.23E-06	0.21	293.56
Overall		32.33	238.27	6.76			
72501001	1	34.76	248.90	13.15	4.01E-06	0.67	285.74
72503001	3	38.87	275.34	9.84	2.26E-06	0.38	288.69
72510001	10	40.28	284.36	9.03	3.08E-06	0.52	289.34
Overall		33.89	244.76	10.91			
92201001	1	54.20	367.47	9.89	5.32E-07	0.09	289.83
92203001	3	49.73	342.17	7.61	1.91E-06	0.32	289.91
92210001	10	45.94	321.80	5.10	1.05E-06	0.18	291.59
Overall		40.26	285.38	7.45			

can be deduced from the columns, which contain the optimized activation energies for an averaged $\ln k_0$ -value. For $n=1/2$ an activation energy of 236 kJ mol⁻¹ is found that differs only by $\pm 2\%$ from the values of single evaluations. The plot of 'compensation' evaluation proves again the close correlation between E_A and $\ln k_0$.

Fig. 8 gives a graphical impression of the evaluation work. One experimental data set (open circles)

is compared with a simulated one (solid line) that was obtained from a non-linear optimization by TA-kin. The differential curve (experiment minus simulation) gives a microscopic picture of the real deviations in the order of 5%. This is truly a convincing example for the abilities of non-linear optimizations of kinetic parameters but not typical for all results. This might support the optimists but scare the pessimists.

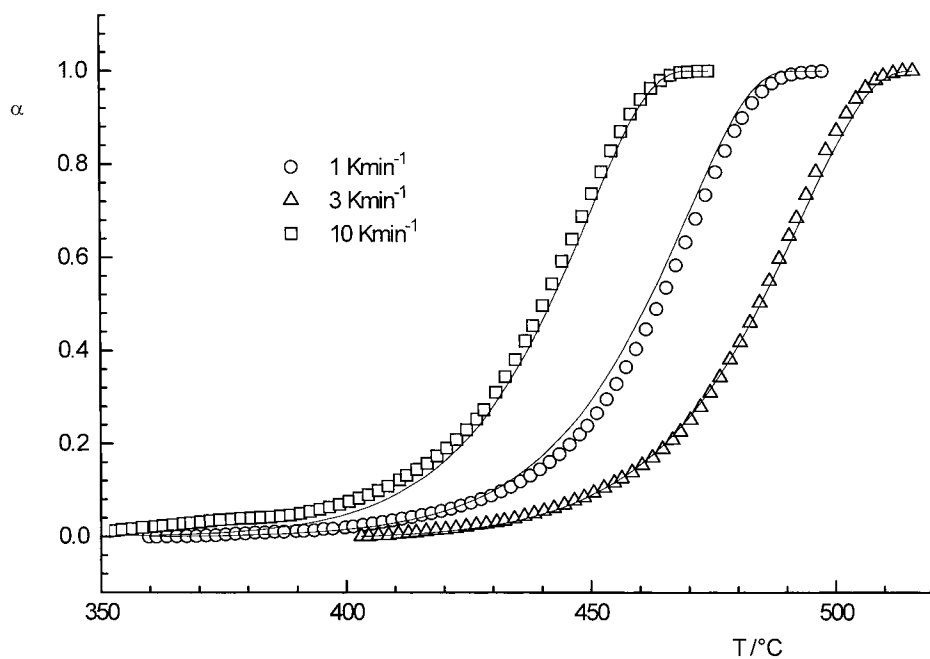


Fig. 7. Overall-evaluation of the second step in inert gas, model F2/3, no. 725, (\circ), (\square), (Δ) measured $\alpha(t)$, (—) simulated $\alpha(t)$.

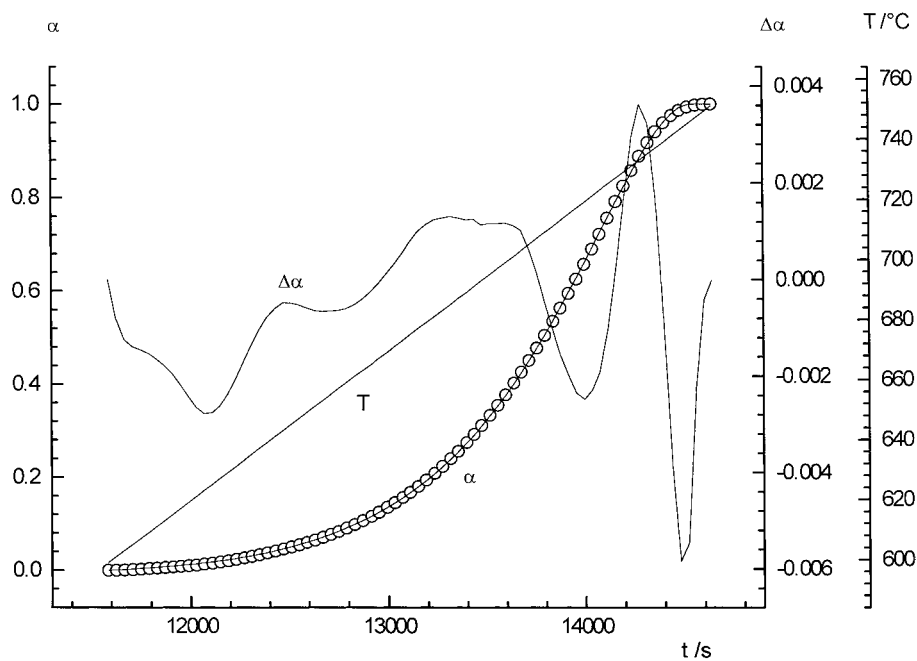


Fig. 8. Evaluation of the third step in air, model F1/2, $\beta=3 \text{ K min}^{-1}$, no. 42103001, (\circ) measured $\alpha(t)$, (—) simulated $\alpha(t)$, (—) calculated $\Delta\alpha(t)$, (—) measured $T(t)$.

Table 8
Evaluation of the third step in air

No.	β (K min ⁻¹)	ln k_0 (s ⁻¹)	E_A (kJ mol ⁻¹)	$1E4^*k(700^\circ\text{C})$ (s ⁻¹)	SDS	Relative SDS	E_A (kJ mol ⁻¹)
<i>(a) Model F1/3 (ln $k_0=19.75$)</i>							
12101001	1	18.30	204.06	9.91	7.59E-08	0.02	214.84
12103001	3	18.58	206.37	9.82	2.44E-08	0.01	215.46
12110001	10	18.27	205.56	8.00	7.71E-08	0.02	217.61
Overall		16.37	189.55	8.59			
22101001	1	22.11	235.78	8.82	5.95E-07	0.13	217.79
22103001	3	22.43	241.94	5.72	1.85E-06	0.40	220.44
22110001	10	21.07	232.38	4.76	1.12E-06	0.24	221.25
Overall		16.25	191.96	5.68			
22101002	1	20.48	227.09	5.06	1.27E-06	0.27	221.44
22103002	3	16.60	196.36	4.67	3.53E-07	0.08	221.59
22110002	10	19.30	219.71	3.88	9.65E-07	0.21	223.48
Overall		18.49	212.09	4.41			
32401001	1	18.17	205.14	7.56	4.07E-07	0.09	217.07
32403001	3	18.16	205.13	7.55	3.79E-07	0.08	217.52
32410001	10	15.62	181.69	10.75	4.65E-06	1.00	215.03
Overall		18.33	205.47	8.52			
42101001	1	25.28	259.13	11.76	3.38E-06	0.73	217.05
42103001	3	21.79	235.39	6.76	4.85E-07	0.10	219.09
42110001	10	20.26	224.06	5.89	8.55E-07	0.18	219.82
Overall		20.12	221.40	7.13			
72103001	3	19.51	213.46	10.33	8.21E-08	0.02	215.33
<i>(b) Model F1/2, relative SDS relates to (a), no. 32410001 (ln $k_0=22.09$)</i>							
12101001	1	20.80	222.16	12.90	5.87E-07	0.13	231.83
12103001	3	20.84	223.32	11.57	3.31E-07	0.07	233.10
12110001	10	20.08	219.69	8.52	3.61E-07	0.08	236.17
Overall		17.10	194.57	9.57			
22101001	1	24.66	254.57	11.05	4.26E-07	0.09	235.03
22103001	3	22.24	239.68	6.22	6.90E-07	0.15	238.50
22110001	10	21.72	237.07	5.09	8.43E-07	0.18	240.23
Overall		16.96	196.96	6.21			
22101002	1	22.84	244.74	6.09	1.03E-06	0.22	238.92
22103002	3	19.21	216.58	5.21	8.37E-07	0.18	239.73
22110002	10	21.53	237.82	3.85	1.24E-06	0.27	242.58
Overall		17.88	206.49	4.80			
32401001	1	20.71	223.70	9.70	2.17E-07	0.05	234.16
32403001	3	20.54	223.08	8.85	3.22E-07	0.07	235.23
32410001	10	21.21	226.24	11.74	5.38E-07	0.12	233.36
Overall		22.75	239.41	10.75			
42101001	1	30.09	295.21	16.76	1.28E-06	0.28	234.29
42103001	3	24.28	254.56	7.60	4.24E-08	0.01	237.12
42110001	10	20.81	227.96	6.33	3.93E-07	0.08	238.64
Overall		17.74	202.02	7.26			
72103001	3	21.91	231.61	12.15	5.60E-07	0.12	233.02

Table 8 (Continued)

No.	β (K min ⁻¹)	ln k_0 (s ⁻¹)	E_A (kJ mol ⁻¹)	$1E4^*k(700^\circ\text{C})$ (s ⁻¹)	SDS	Relative SDS	E_A (kJ mol ⁻¹)
(c) Model F2/3, relative SDS relates to (a), no. 32410001 (ln $k_0=24.56$)							
12101001	1	23.20	239.48	16.62	1.73E-06	0.37	249.71
12103001	3	23.15	240.66	13.65	1.23E-06	0.26	251.70
12110001	10	22.32	237.32	9.01	1.23E-06	0.27	255.73
Overall		17.79	199.34	10.62			
22101001	1	27.35	274.49	13.95	8.06E-07	0.17	253.20
22103001	3	24.63	258.11	6.96	1.75E-06	0.38	257.55
22110001	10	24.32	258.19	5.04	2.09E-06	0.45	260.23
Overall		17.64	201.74	6.79			
22101002	1	25.31	263.15	7.35	1.38E-06	0.30	257.36
22103002	3	21.43	233.73	5.79	2.07E-06	0.45	258.85
22110002	10	23.83	256.57	3.80	2.35E-06	0.51	262.71
Overall		18.59	211.57	5.21			
32401001	1	23.18	241.75	12.37	8.94E-07	0.19	252.17
32403001	3	22.90	240.90	10.37	1.02E-06	0.22	253.91
32410001	10	23.54	244.36	12.74	1.73E-06	0.37	252.68
Overall		23.52	244.75	11.99			
42101001	1	33.10	317.54	21.49	5.60E-07	0.12	252.43
42103001	3	27.08	276.23	8.59	4.01E-07	0.09	256.13
42110001	10	23.17	246.89	6.47	1.23E-06	0.27	258.46
Overall		18.59	208.08	8.00			
72103001	3	24.43	250.65	14.33	1.69E-06	0.36	251.67

For the inert gas experiments of the CO₂-split-off the TG data sets were again evaluated by the formal kinetic model F_n with $n=1/3$, $1/2$ and $2/3$, respectively. For the majority of all optimization trials the most suitable reaction order was found to be $n=1/2$, (see Table 9(b)). The relative SDS values point to this direction. As for the second reaction step, even for the third step smaller activation energies were observed in inert gas than in air.

6. Conclusions

Within the expected scope of the possibilities of kinetic evaluations in thermal analysis the results of the round robin test can be appraised as satisfactory in comparison to the widespread prejudices against the active trials of serious kinetic workers in this field. The authors agree with the doubts of some authors about application of kinetics to TA experiments, which are

performed under insufficiently defined or incomparable preconditions. Such experiments should not be a subject of kinetic evaluation procedures. Of course it is only possible to find successfully reliable results if the prerequisites relating to

- the investigated material,
- the experimental technique and
- the applied non-linear evaluation procedure

are well defined and fixed.

New hope arises from the fact that in the present RRT only the first and the third points were clearly defined. Whereas the experimental technique was not restricted at all delegating the responsibility to the experimenter. This was possible because only laboratories with a corresponding know-how were invited to measure. This turned out to be one of the roots for the favorable course of this teamwork.

Table 9
Evaluation of the third step in inert gas

No.	β (K min ⁻¹)	ln k_0 (s ⁻¹)	E_A (kJ mol ⁻¹)	$1E4^*k(700^\circ\text{C})$ (s ⁻¹)	SDS	Relative SDS	E_A (kJ mol ⁻¹)
<i>(a) Model F1/3, relative SDS relates to (c), no. 22310002 (ln $k_0=19.47$)</i>							
12201001	1	20.99	211.78	56.03	1.92E-07	0.04	200.98
12203001	3	20.70	209.85	53.21	1.04E-07	0.02	200.79
12210001	10	23.20	232.87	37.52	2.70E-06	0.62	203.70
Overall		18.26	192.95	37.54			
22301001	1	17.91	201.09	9.63	7.04E-07	0.16	212.82
22303001	3	18.52	206.44	9.17	5.59E-07	0.13	213.88
22310001	10	18.71	206.25	11.37	3.00E-06	0.69	212.42
Overall		20.07	217.72	10.71			
22301002	1	16.45	194.99	4.77	2.24E-07	0.05	218.18
22303002	3	17.37	203.16	4.36	3.82E-07	0.09	220.02
22310002	10	17.08	201.02	4.25	9.12E-07	0.21	221.18
Overall		16.11	192.74	4.46			
42301001	1	19.65	215.71	8.99	9.79E-07	0.23	214.39
42303001	3	19.29	214.02	7.78	5.92E-07	0.14	215.42
42310001	10	18.65	207.91	8.68	9.91E-07	0.23	214.64
Overall		19.56	215.56	8.40			
72501001	1	20.59	211.65	38.11	1.86E-07	0.04	203.60
72503001	3	19.89	206.96	33.96	2.70E-07	0.06	203.80
72510001	10	19.53	204.24	33.07	7.37E-07	0.17	203.78
Overall		20.41	210.74	35.61			
92201001	1	20.23	226.68	4.16	1.47E-07	0.03	220.76
92203001	3	21.62	238.36	3.93	9.12E-07	0.21	220.97
92210001	10	20.16	226.88	3.76	5.72E-07	0.13	221.12
Overall		20.09	225.95	3.97			
<i>(b) Model F1/2, relative SDS relates to (c), no. 22310002 (ln $k_0=22.35$)</i>							
12201001	1	23.57	229.53	82.34	3.36E-07	0.08	220.86
12203001	3	23.10	226.90	70.99	1.40E-07	0.03	221.40
12210001	10	27.76	268.04	46.73	1.27E-06	0.29	225.60
Overall		17.07	183.48	36.71			
22301001	1	21.98	231.07	13.93	4.89E-07	0.11	233.84
22303001	3	21.82	231.63	11.03	5.02E-07	0.12	235.80
22310001	10	22.31	234.87	12.12	1.52E-06	0.35	235.18
Overall		20.77	222.53	11.86			
22301002	1	18.53	210.25	5.75	4.51E-07	0.10	239.68
22303002	3	19.95	223.23	4.84	8.87E-07	0.20	242.51
22310002	10	19.22	218.34	4.24	2.05E-06	0.47	244.78
Overall		16.53	195.53	4.84			
42301001	1	23.29	242.67	12.29	2.74E-07	0.06	235.55
42303001	3	21.55	231.12	8.94	2.32E-07	0.05	237.48
42310001	10	21.64	231.75	9.12	3.14E-07	0.07	237.55
Overall		19.99	218.30	9.21			

Table 9 (Continued)

No.	β (K min ⁻¹)	ln k_0 (s ⁻¹)	E_A (kJ mol ⁻¹)	$1E4^*k(700^\circ\text{C})$ (s ⁻¹)	SDS	Relative SDS	E_A (kJ mol ⁻¹)
72501001	1	23.78	234.05	58.16	2.29E-07	0.05	223.74
72503001	3	22.36	224.78	44.24	1.13E-07	0.03	224.70
72510001	10	22.00	222.82	39.28	1.86E-07	0.04	225.56
Overall		20.26	209.02	38.02			
92201001	1	22.55	244.10	4.93	7.71E-07	0.18	242.52
92203001	3	24.72	262.80	4.25	8.78E-07	0.20	243.62
92210001	10	22.11	242.63	3.79	1.20E-06	0.28	244.67
Overall		20.26	226.58	4.32			
(c) Model F2/3 (ln $k_0=24.81$)							
12201001	1	26.13	247.18	120.54	1.14E-06	0.26	237.77
12203001	3	25.59	244.72	95.40	8.37E-07	0.19	238.94
12210001	10	30.70	290.43	55.29	1.25E-06	0.29	244.22
Overall		17.68	187.44	41.40			
22301001	1	24.52	249.49	18.01	1.54E-06	0.36	251.71
22303001	3	24.31	250.51	12.92	1.32E-06	0.30	254.44
22310001	10	24.93	255.49	12.97	1.16E-06	0.27	254.52
Overall		21.52	227.80	13.17			
22301002	1	20.85	227.42	7.02	1.30E-06	0.30	257.96
22303002	3	22.20	240.64	5.34	2.17E-06	0.50	261.63
22310002	10	21.43	236.30	4.22	4.33E-06	1.00	264.85
Overall		17.12	199.62	5.25			
42301001	1	25.90	261.81	15.70	4.66E-07	0.11	253.54
42303001	3	23.92	249.23	10.29	6.68E-07	0.15	256.23
42310001	10	23.93	249.79	9.64	5.58E-07	0.13	257.03
Overall		20.83	224.23	10.22			
72501001	1	26.30	251.63	82.33	9.51E-07	0.22	240.88
72503001	3	24.83	242.64	57.58	7.24E-07	0.17	242.48
72510001	10	24.33	240.31	46.33	3.42E-07	0.08	244.09
Overall		21.12	214.79	43.81			
92201001	1	25.02	262.65	5.85	2.06E-06	0.48	261.03
92203001	3	27.16	281.97	4.60	1.59E-06	0.37	262.87
92210001	10	24.52	262.25	3.73	2.37E-06	0.55	264.72
Overall		21.08	232.59	4.71			

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

The following TA-laboratories took part in the round robin test:

- D. Schultze, BAM Berlin
- A.A. Kossoy and A.S. Benin, GIPH St. Petersburg, Russia
- G.K. Leitner and K. Jaenicke-Rößler, IKTS Dresden
- M. Epple, Universität Hamburg
- E. Marti, Ciba-Geigy AG, Switzerland
- S. Goth and E. Wasmer, Perkin-Elmer, Ueberlingen
- E. Post and J. Henderson, Applikationslabor Netzsch, Selb/Bavaria
- H.J. Flammersheim and N. Eckardt, Universität Jena

- G.W.H. Höhne and J.E.K. Schawe, Universität Ulm
- A. Baumgarte, ETH Zürich, Switzerland
- S. Neuenfeld, Merck KGaA, Darmstadt
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