Computational aspects of kinetic analysis
Part A: The ICTAC kinetics project-data, methods and results[☆]

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Abstract

Part A of this series of papers (Parts B to E follow) presents the data and methods used, as well as the results obtained by participants in the ICTAC Kinetics Project. The isothermal and non-isothermal data sets provided were based on a hypothetical simulated process as well as on some actual experimental results for the thermal decompositions of ammonium perchlorate and calcium carbonate. The participants applied a variety of computational methods. Isoconversional and multi-heating rate methods were particularly successful in correctly describing the multi-step kinetics used in the simulated data. Reasonably consistent kinetic results were obtained for isothermal and non-isothermal data. There is, of course, no 'true' answer for the kinetic parameters of the real data, so the findings of the participants are compared. An attempt has been made to forecast the tendencies for the future development of solid state kinetics. © 2000 Elsevier Science B.V. All rights reserved.

[☆]Part A has been substantially agreed by the authors named, but all other parts are the opinions of the author(s) of that part only; although the Project was initiated by the International Confederation for Thermal Analysis and Calorimetry, ICTAC, the views expressed are not necessarily representative of ICTAC or any of its committees.

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1. Introduction

Solid state kinetics are extensively studied by thermal analysis methods. Kinetic analysis of the data produced has been the subject of numerous criticisms. The positive impact of these criticisms has been that the limitations of kinetic analyses have been under scrutiny. Unfortunately, the criticisms have also inspired a somewhat pessimistic attitude toward solid-state kinetics that has negatively affected the field. Nevertheless, solid state kinetics has continued to develop together with improvements in both experimental and computational methods.

The quality of experimental data has improved steadily with the instrumentation available. The performance characteristics of a measuring system (noise, repeatability, linearity, time constant and sensitivity) have been reviewed by Hemminger and Sarge [1]. Use of small samples has decreased the problems of heat transfer at the expense of a possible decrease in the homogeneity of the sample. Inadequate reproducibility of data for a decomposition is almost always traceable to the sample rather than to the instrument used.

It is now recognised [2,3] that real solid state reactions are often too complex to be described in terms of a single pair of Arrhenius parameters and the traditional set of reaction models. This has inspired development of new computational techniques that make allowance for multi-step kinetics.

Although new ideas and techniques continue to emerge, the arrival of the new millennium has been used to attempt to mark some of the progress made in the area of kinetic analysis of solid state reactions. This progress seems to have been adequately mirrored in the results of the ICTAC Kinetics Project [4,5], which are presented in this series of papers. Part A describes the computational methods used and the kinetic results obtained by the participants in the Project. Parts B and C present detailed individual discussions, by two of the *organizers* of the Project, of the kinetic results described in Part A. Parts D and E are individual points-of-view provided by two of the *participants* in response to an invitation to all participants.

A full kinetic analysis of a solid state reaction has at least three major stages: (1) Experimental collection of data; (2) Computation of kinetic characteristics for the data from stage 1; and (3) Interpretation of the

significance of any parameters evaluated in stage 2. Motives for carrying out such an analysis may range from practical needs to predict behaviour under untested conditions from the results collected, to general theoretical considerations of the factors determining thermal stability and/or reactivity of solids.

1.1. Experimental stage

The design and execution of a series of experiments to collect data suitable for adequate kinetic analysis requires many decisions from the researcher. Should the sample be a powder or a single crystal? How does one obtain a representative sample? How does one characterise the sample used? Will experiments be done under isothermal, or programmed temperature, or controlled-rate conditions? Is the reaction reversible and, if so, what conditions are needed to ensure negligible contribution from the reverse reaction? What are the heat transfer conditions estimated to be — will self-heating or self-cooling be a possible problem? Does the reaction actually take place in the solid state or is there any indication of melting? Is there any evidence for reaction with the surrounding gaseous atmosphere? The answers to some of these questions may have to be deduced after examination of the outcome of Stage 2.

1.2. Computational stage

On the assumptions that the data obtained in Stage 1 are reliable and that random noise in the data is negligible, one can proceed in the search for a mathematical description of the data. From the experimental options available in Stage 1, the data will usually be in one of the following forms:

1. Sets of α, t (or $d\alpha/dt$, t) data at several different constant temperatures. (Sometimes temperature jumps are carried out during the course of a single decomposition).
2. Sets of α, T (or $d\alpha/dt$, T or $d\alpha/dT$, T) data at several different constant heating rates, β.
3. Sets of T, t data obtained at several different constant reaction rates, $d\alpha/dt$.

The search for a mathematical description of the data is usually sought in terms of a 'kinetic triplet' (i.e., Arrhenius parameters A and E_a, and the reaction

model, $f(\alpha)$, also called the conversion function) which is related to the experimental data as follows

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha)$$

For non-isothermal data obtained at a constant heating rate $\beta = dT/dt$, $d\alpha/dt$ in the above equation is replaced with $\beta\, d\alpha/dT$. The above equation may, however, be extended to cater for more complex processes such as concurrent or consecutive reactions, each with its own kinetic triplet. Such an extension is an admission that more adjustable parameters may be required to provide a realistic description of decomposition in the solid state.

1.3. Interpretation

This last stage is undoubtedly the most difficult because all the accumulated evidence, and the accompanying accumulated uncertainties, have to be assessed. Attempts have to be made to relate the computational results to the actual sequence of physico-chemical processes occurring, i.e. the reaction mechanism. Formulation of such a relationship is generally only possible with the aid of complementary information from microscopic, spectroscopic and structural studies. A prerequisite for establishing such a relationship is the use of an adequate computational method for treatment of experimental data.

2. The ICTAC kinetics project

Arising from the Kinetics Workshop, held during the 11th International Congress on Thermal Analysis and Calorimetry (ICTAC) in Philadelphia, USA, in August 1996, sets of kinetic data were prepared and distributed to volunteer participants for their analysis using any, or several, methods they wished.

The data sets [4,5] were as follows:

- Set 1: (Fig. 1) six experimental alpha-temperature curves for the decomposition of calcium carbonate (CC) in vacuum, obtained at different heating rates (1.8, 2.5, 3.5, 5.0, 6.2 and 10 K min^{-1} as shown), FILE: CCVKPM.TXT (Table 1).
- Set 2: (Fig. 2) six experimental alpha-temperature curves for the decomposition of calcium carbonate (CC) in nitrogen, obtained at different heating

Fig. 1. Six experimental alpha-temperature curves for the decomposition of calcium carbonate (CC) in vacuum, obtained at different heating rates (1.8, 2.5, 3.5, 5.0, 6.2 and 10 K min^{-1}).

rates (1.0, 3.0, 5.0, 7.5, 10, 15 and 25 K min^{-1} as shown), FILE: CCNKPM.TXT (Table 2).
- Set 3: (Fig. 3) six experimental alpha-time curves for the decomposition of calcium carbonate (CC) in vacuum, obtained at different temperatures (550, 540, 535, 530, 520 and 515°C as shown), FILE: CCVISO.TXT (Table 3).
- Set 4: (Fig. 4) seven experimental alpha-time curves for the decomposition of calcium carbonate (CC) in nitrogen, obtained at different

Fig. 2. Six experimental alpha-temperature curves for the decomposition of calcium carbonate (CC) in nitrogen, obtained at different heating rates (1.0, 3.0, 5.0, 7.5, 10, 15 and 25 K min^{-1}).
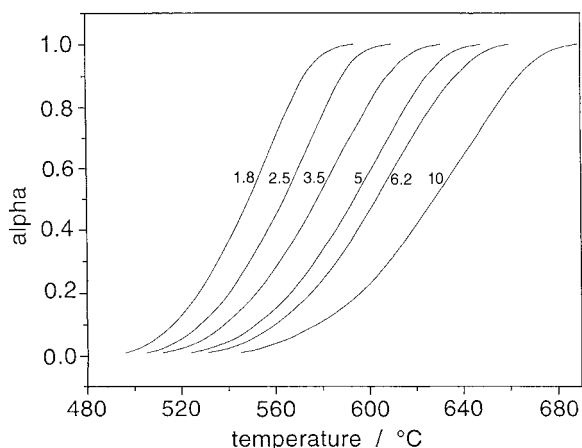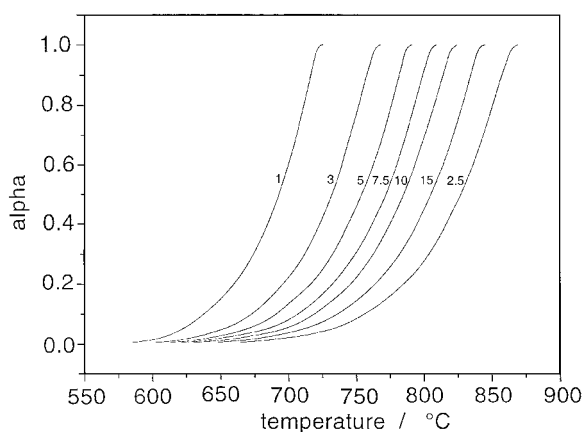
Table 1
Set 1: (see also Fig. 1) six experimental alpha-temperature curves for the decomposition of calcium carbonate (CC) in vacuum, obtained at different heating rates (1.8, 2.5, 3.5, 5.0, 6.2 and 10 K min^{-1}), FILE: CCVKPM.TXT

Contributor	Method	E_a/kJ mol^{-1}	ln (A/s^{-1})
Anderson	TA-KIN for Windows 1.6		
	Reaction order $n=0.5$	120.2	10.05
	Consecutive reactions		
	Step 1: $n=0.5$	108.8	8.64
	Step 2: $n=1.0$	107.1	10.27
Burnham	Friedman $n=1$		
	Low α	106±7	7.89
	High α	89±15	7.07
	Coats-Redfern (modified)		
	Low α	144±2	12.65
	High α	110±2	9.15
	First-order (Kissinger)	122±2	10.28
	Nucleation NLR (Sestak–Berggren)		
	($m=0.592$; $n=1.000$; $q=0.99$)	116.1	10.50
	($m=0.511$; $n=0.825$; $q=0.99$)	115.7	10.22
	($m=0.411$; $n=0.761$; $q=0.99999$)	115.6	10.08
Desseyn et al.	Kofstad		
	Low heating-rate, $\beta=1.8$	233	27.2
	High heating-rate, $\beta=10$	178	18.07
	Ingraham and Marrier		
	Low heating-rate, $\beta=1.8$	240	21.50
	High heating-rate, $\beta=10$	181	11.71
	Freeman and Carroll		
	Low heating-rate, $\beta=1.8$	223	−8.7
	High heating-rate, $\beta=10$	147	−7.46
	General		
	Low heating-rate, $\beta=1.8$	60	–
	High heating-rate, $\beta=10$	58	–
	Friedman $n=1.46$		8.66
	Low α	121	
	High α	90	
	Ozawa		
	Low α	168	
	High α	123	
Nomen and Sempere	Non-parametric method		
	Sestak–Berggren ($n=0.709±0.004$; $m=0.348±0.004$)	106.3±0.3	8.68±0.03
Opfermann	Friedman		
	Low α	134±13	11.58
	High α	92±11	7.46
	Flynn, Wall, Ozawa		
	Low α	162±4	14.44
	High α	110±2	9.35
	Multivar-NLR		
	n-dim Avrami		
	($n=1.627±0.011$)	109.6±0.7	8.80±0.11
	Consecutive reactions		
	Step 1: n-dim Avrami		
	($w=0.083$, $n=1.28±0.14$)	134±15	13.1±2.5
	Step 2: nth order		
	($w=0.917$, $n=0.543±0.040$)	94±4	6.74±0.45

Table 1 (*Continued*)

Contributor	Method	E_a/kJ mol^{-1}	ln (A/s^{-1})
Roduit	Friedman		
	α=0.1	105±17	
	α=0.9	90±30	
	Flynn, Wall, Ozawa		
	α=0.1	145±4	
	α=0.9	115±4	
	Multivar-NLR		
	n-dim Avrami		
	w=0.7091 (n=2.451±0.049)	102.74±0.14	7.51±0.02
	w=0.2909 (n=1.294±0.014)	204.88±0.15	22.85±0.05
Li and Tang	Flynn, Wall, Ozawa		
	Low α to high α	138±20	
	Kissinger, Akahira and Sunrose		
	Low α to high α	130±22	
	Friedman		
	Low α to high α	102±13	
	Li and Tang		
	Low α to high α	112±8	

Table 2

Set 2: (see also Fig. 2) six experimental alpha-temperature curves for the decomposition of calcium carbonate (CC) in nitrogen, obtained at different heating rates (1.0, 3.0, 5.0, 7.5, 10, 15 and 25 K min^{-1}), FILE: CCNKPM.TXT

Contributor	Method	E_a/kJ mol^{-1}	ln (A/s^{-1})
Anderson	TA-KIN for Windows 1.6		
	Reaction order *n*=0 (diffusion)	191	15.4
Burnham (β=7.5 and 15 K min^{-1} omitted)	Friedman *n*=1	192±5	16.0±1.0
	Coats-Redfern (modified)	195±3	16.5±1.3
	Nucleation NLR (Sestak–Berggren)		
	(m=0.011; n=0.176)	194.9	15.96
Desseyn et al.	Kofstad		
	Low heating-rate, β=1	166	16.24
	High heating-rate, β=25	196	20.18
	Ingraham and Marrier		
	Low heating-rate, β=1	170	9.97
	High heating-rate, β=25	199	13.58
	Freeman and Carroll		
	Low heating-rate, β=1	131	−5.91
	High heating-rate, β=25	163	−3.20
	General		
	Low heating-rate, β=1	162	–
	High heating-rate, β=15	173	–
	Friedman *n*=−0.187		15.3
	Low α	178	
	High α	197	
	Ozawa		
	Low α	223	
	High α	211	
Nomen and Sempere	Non-parametric method		
	(n=0.126±0.002)	181.4±0.3	14.32±0.04

Table 2 (*Continued*)

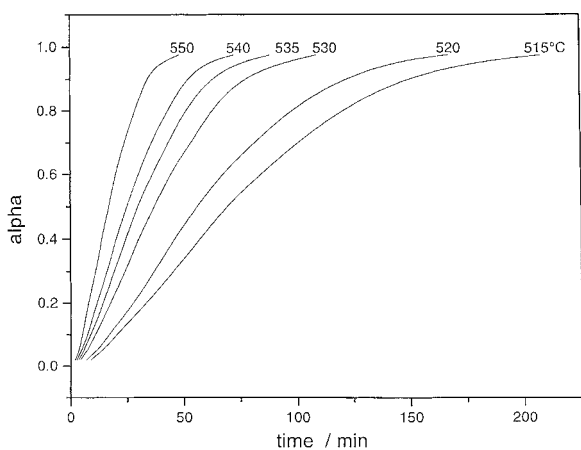| Contributor	Method	E_a/kJ mol^{-1}	ln (A/s^{-1})
Opfermann	Friedman		
	Low α	183±7	14.44
	High α	176±11	16.58
	Flynn, Wall, Ozawa		
	Low α	219±12	18.84
	High α	194±2	17.02
	Multivar-NLR		
	nth order (n=0.146±0.008)	192.6±0.2	15.75±0.02
	Consecutive reactions		
	Step 1: (n=1, w=0.038)	134±4	10.34±0.48
	Step 2: (n=0.164±0.014, w=0.962)	197.9±0.2	16.33±0.02
Roduit	Friedman		
	α=0.1	190±12	
	α=0.9	195±11	
	Flynn, Wall, Ozawa		
	α=0.1	199±7	
	α=0.9	194±7	
	ASTM	197±24	
	Multivar-NLR		
	contracting geometry		
	n=1.215±0.021 or nth order	194.26±0.18	15.67±0.04
	n=0.177±0.011	194.26±0.18	15.86±0.04
Li and Tang	Flynn, Wall, Ozawa		
	Low α to high α	202±4	
	Kissinger, Akahira and Sunrose		
	Low α to high α	197±5	
	Friedman		
	Low α to high α	188±10	
	Li and Tang		
	Low α to high α	193±2	

Fig. 3. Six experimental isothermal alpha-time curves for the decomposition of calcium carbonate (CC) in vacuum, obtained at different temperatures (550, 540, 535, 530, 520 and 515°C).
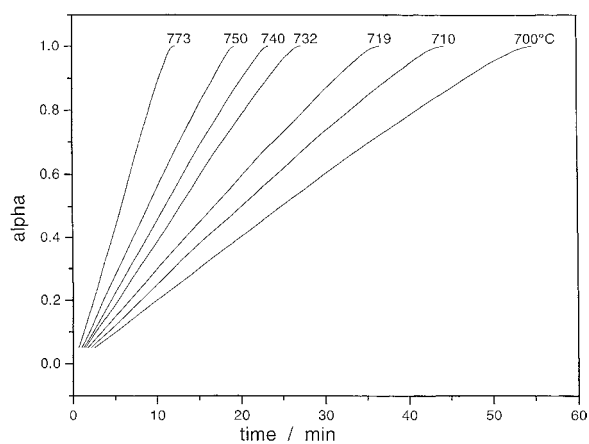

Fig. 4. Seven experimental isothermal alpha-time curves for the decomposition of calcium carbonate (CC) in nitrogen, obtained at different temperatures (773, 750, 740, 732, 719, 710 and 700°C).

Table 3
Set 3: (see also Fig. 3) six experimental isothermal alpha-time curves for the decomposition of calcium carbonate (CC) in vacuum, obtained at different temperatures (550, 540, 535, 530, 520 and 515°C), FILE: CCVISO.TXT

Contributor	Method	E_a/kJ mol^{-1}	ln (A/s^{-1})
Anderson	TA-KIN for Windows 1.6		
	Reaction order n=0.5	219.8	24.78
	Consecutive reactions		
	Step 1: n=0.5	227.2	25.96
	Step 2: n=1.0	120.0	32.10
Burnham	Friedman n=1		
	Low α	221±14	24.91
	High α	262±12	32.10
	Nucleation NLR (Sestak–Berggren)		
	(m=0.495; n=1.00)	221.7	25.94
Desseyn et al.	Isothermal method (n=1) (irregularly with α)	195 to 262	21.3 to 36.25
Opfermann	Multivar-NLR		
	n-dim Avrami n=1.5543	222.8±0.4	11.04±0.03
Roduit	Multivar-NLR		
	n-dim Avrami n=1.527±0.038	224.24±0.10	25.66±0.09
Set 1+Set 3			
Opfermann	Multivar-NLR		
	n-dim Avrami n=1.404±0.066	142.8±1.8	13.43±0.27
	Consecutive reactions		
	Step 1: n-dim Avrami		
	(w=0.0186, n=1.345±0.048)	220.5±1.9	25.13±0.29
	Step 2: nth order		
	(w=0.9814, n=0.016±0.018)	75.9±0.6	3.68±0.09
Malek and Mitsuhashi	n-dim Avrami n=1.7		
	(0.3<α<0.7)	104±4	

temperatures (773, 750, 740, 732, 719, 710 and 700°C as shown), FILE: CCNISO.TXT (Table 4).

- Set 5: (Fig. 5) six experimental alpha-temperature curves for the decomposition of ammonium perchlorate (AP) in nitrogen, obtained at different heating rates (a=2.52, b=5.16, c=7.58, d=10.49, e=12.79 and f=15.45 K min^{-1}), FILE: APKPM.TXT (Table 5).
- Set 6: (Fig. 6) five isothermal alpha-time curves for the decomposition of ammonium perchlorate (AP) in flowing nitrogen, obtained at different temperatures (a=558, b=553, c=548, d=543 and e=538 K), FILE: APISO.TXT (Table 6).
- Set 7: (Fig. 7) five simulated alpha-temperature curves calculated at heating rates of 0.5, 1.0, 2.0, 4.0 and 8.0 K min^{-1}, FILE: SIMKPM.TXT (Table 7).
- Set 8: (Fig. 8) five simulated isothermal alpha-time curves calculated at temperatures of a=380,

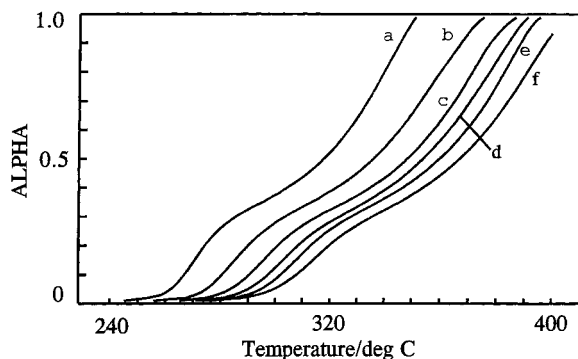b=375, c=370, d=365 and e=360 K, FILE: SIMISO.TXT (Table 8).

Fig. 5. Six experimental alpha-temperature curves for the decomposition of ammonium perchlorate (AP) in nitrogen, obtained at different heating rates (a=2.52, b=5.16, c=7.58, d=10.49, e=12.79 and f=15.45 K min^{-1}).

Table 4
Set 4: (see also Fig. 4) seven experimental isothermal alpha-time curves for the decomposition of calcium carbonate (CC) in nitrogen, obtained at different temperatures (773, 750, 740, 732, 719, 710 and 700°C), FILE: CCNISO.TXT

Contributor	Method	E_a/kJ mol^{-1}	ln (A/s^{-1})
Anderson	TA-KIN for Windows 1.6		
	Reaction order $n=0$	175	13.6
Burnham (773, 732 and 700 K only.)	Friedman $n=1$ ($\alpha=0.5$)	190.3±0.3	16.18
	Nucleation NLR (Sestak–Berggren)		
	($m=0.087; n=0.155$)	180.3	14.44
Desseyn et al.	Isothermal method	156–183 (with α)	11.3–16.79
Opfermann	Multivar-NLR		
	nth order ($n=0.067±0.007$)	178.09±0.06	14.00±0.01
Roduit	Multivar-NLR		
	Contracting geometry		
	$n=1.101±0.009$ or nth order	181.01±0.09	14.28±0.02
	$n=0.092±0.009$	181.01±0.09	14.38±0.02
Set 2+Set 4			
Anderson	TA-KIN for Windows 1.6	184	14.7
Burnham	Friedman $n=1$ ($\alpha=0.5$)	188±10	15.76
	Nucleation NLR (Sestak–Berggren)		
	($m=0.117; n=0.222$)	190.9	15.75
Opfermann	Multivar-NLR		
	nth order ($n=0.060±0.009$)	187.5±0.5	15.09±0.06
Malek and Mitsuhashi	nth order $n=0.1$		
	($0.3<\alpha<0.7$)	103±3	

The data sets 7 and 8 were simulated using a system of two equally-weighted, parallel, first-order reactions:

$$\frac{d\alpha}{dt} = \frac{1}{2}\left(\frac{d\alpha_1}{dt} + \frac{d\alpha_2}{dt}\right)$$
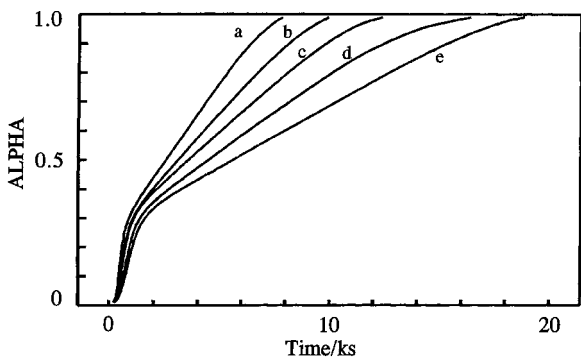$$= \frac{1}{2}[k_1(T)(1-\alpha_1) + k_2(1-\alpha_2)]$$

Fig. 6. Five isothermal alpha-time curves for the decomposition of ammonium perchlorate (AP) in flowing nitrogen, obtained at different temperatures ($a=558$, $b=553$, $c=548$, $d=543$ and $e=538$ K).
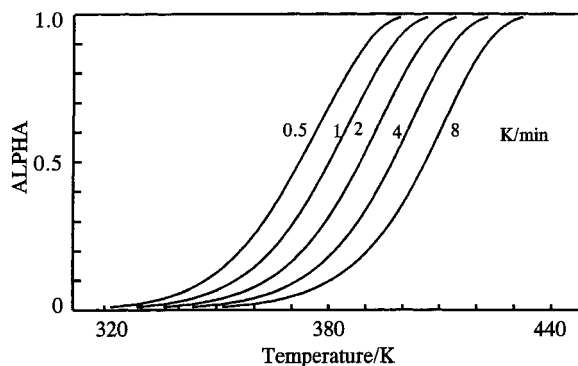

Fig. 7. Five simulated alpha-temperature curves calculated at heating rates of 0.5, 1.0, 2.0, 4.0 and 8.0 K min^{-1}.

Table 5
Set 5: (see also Fig. 5) six experimental alpha-temperature curves for the decomposition of ammonium perchlorate (AP) in nitrogen, obtained at different heating rates (a=2.52, b=5.16, c=7.58, d=10.49, e=12.79 and f=15.45 K min^{-1}), FILE: APKPM.TXT

Contributor	Method	E_a/kJ mol^{-1}	ln (A/s^{-1})
Burnham	Friedman n=1		
(2.52, 7.58, 15.45 K min^{-1} only)	Low α=0.1	79.4±0.3	10.27
	High α=0.4	115±4	16.24
	Coats-Redfern (modified)		
	Low α=0.3	93.0±1.2	12.59
	High α=0.9	109±4	15.62
	First-order (Kissinger)	116±10	16.21
	nth-order; n=0.331	116±10	16.21
	Concurrent Sestak–Berggren processes (NLR)		
	Step 1: w=0.270		
	m=1.00, n=1.81	97.7	17.11
	Step 2: w=0.730		
	m=0, n=0.294	113.0	15.59
Nomen and Sempere	Non-parametric method		
	Consecutive Sestak–Berggren processes		
	Step 1: w=0.46		
	n=3.53, m=0.98	75.8	12.50
	Step 2: w=0.54		
	n=0.38, m=0.33	121	15.42
Opfermann	Friedman		
	Low α=0.1	82.4±3.6	15.04
	High α=0.6	117.5±5.0	21.02
	Flynn, Wall, Ozawa		
	Low α=0.3	94.7±2.3	13.01
	High α=0.9	114.5±5.2	16.67
	ASTM E698	116.4±7.1	16.93
	Multivar-NLR		
	Concurrent reactions		
	Step 1: n-dim Avrami		
	(w=0.232, n=2.26±0.17)	92.0±2.6	14.15±0.57
	Step 2: nth order		
	(w=0.768, n=0.354±0.028)	113.43±0.88	15.58±0.13
	Consecutive reactions		
	Step 1: n-dim Avrami		
	(w=0.251, n=2.11±0.12)	93.0±2.7	14.39±0.58
	Step 2: nth order		
	(w=0.749, n=0.363±0.026)	113.43±0.88	15.76±0.17
	Concurrent reactions		
	Step 1: first-order with autocatalysis		
	(w=0.232, ln k_{cat}=3.02±0.28)	91.8±2.9	12.33±0.60
	Step 2: nth order		
	(w=0.768, n=0.354±0.026)	112.62±0.87	15.58±0.17
	Consecutive reactions		
	Step 1: first-order with autocatalysis		
	(w=0.251, ln k_{cat}=2.79±0.25)	93.3±2.5	12.87±0.47
	Step 2: nth order		
	(w=0.749, n=0.365±0.027)	113.44±0.68	15.76±0.13
Roduit	Friedman		
	α=0.1	83±12	
	α=0.9	117±38	

Table 5 (*Continued*)

Contributor	Method	E_a/kJ mol^{-1}	ln (A/s^{-1})
	Flynn, Wall, Ozawa		
	α=0.1	108±7	
	α=0.9	114±14	
	ASTM		
	α<0.5	100±15	
	α>0.5	112±37	
	Multivar-NLR		
	w=0.2211, Avrami		
	n=2.818±0.052	99.49±0.11	15.62±0.16
	w=0.7789 EITHER contracting geometry		
	n=1.876±0.017	112.68±0.13	15.02±0.04
	OR nth order		
	n=0.467±0.007	112.68±0.13	15.65±0.05

Table 6
Set 6: (see also Fig. 6) five isothermal alpha-time curves for the decomposition of ammonium perchlorate (AP) in flowing nitrogen, obtained at different temperatures (a=558, b=553, c=548, d=543 and e=538 K), FILE: APISO.TXT

Contributor	Method	E_a/kJ mol^{-1}	ln (A/s^{-1})
Burnham	Friedman n =1		
	Low α=0.3	72±21	7.31
	High α=0.8	129±18	20.24
	Concurrent Sestak–Berggren processes (NLR)		
	Step 1: w=0.270		
	m=1.00, n=1.33	82.6	13.21
	Step 2: w=0.730		
	m=0, n=0.0615	107.6	14.28
Opfermann	Multivar-NLR		
	Concurrent reactions		
	Step 1: n-dim Avrami		
	(w=0.222, n=3.57±0.34)	66.96±0.76	7.96±0.15
	Step 2: nth order		
	(w=0.778, n=0.192±0.018)	105.76±0.24	14.00±0.05
	Consecutive reactions		
	Step 1: n-dim Avrami		
	(w=0.246, n=3.10±0.22)	66.46±0.83	8.57±0.17
	Step 2: nth order		
	(w=0.754, n=0.202±0.017)	107.86±0.21	14.50±0.04
	Concurrent reactions		
	Step 1: first-order with autocatalysis		
	(w=0.223, ln k_{cat}=4.98±0.16)	67.57±0.31	4.90±0.14
	Step 2: nth order		
	(w=0.777, n=0.191±0.018)	105.76±0.24	14.02±0.06
	Consecutive reactions		
	Step 1: first-order with autocatalysis		
	(w=0.244, ln k_{cat}=4.22±0.27)	74.08±0.82	7.08±0.08
	Step 2: nth order		
	(w=0.756, n=0.204±0.017)	107.71±0.20	14.47±0.04

Table 6 (*Continued*)

Contributor	Method	E_a/kJ mol^{-1}	ln (A/s^{-1})
Roduit	Multivar-NLR		
	w=0.2357, Avrami		
	n=2.922±0.049	99.28±0.12	15.17±0.17
	w=0.7643 EITHER contracting geometry		
	n=1.258±0.019	111.76±0.09	15.10±0.05
	OR nth order		
	n=0.21±0.06	111.76±0.09	15.33±0.09
Set 5 and Set 6			
Opfermann	Multivar-NLR		
	Concurrent reactions		
	Step 1: n-dim Avrami		
	(w=0.237, n=1.39±0.25)	115.4±4.4	18.89±0.96
	Step 2: nth order		
	(w=0.763, n=0.261±0.058)	111.1±0.4	15.21±0.06
	Consecutive reactions		
	Step 1: n-dim Avrami		
	(w=0.256, n=1.36±0.21)	111.2±4.3	18.00±0.91
	Step 2: nth order		
	(w=0.744, n=0.260±0.057)	111.1±0.4	15.23±0.06
	Concurrent reactions		
	Step 1: nth order with autocatalysis		
	(w=0.232, n=0.613±0.604, ln k_{cat}=−0.345)	116.3±6.9	18.7±1.6
	Step 2: nth order		
	(w=0.768, n=0.273±0.037)	111.1±0.5	15.22±0.10
	Consecutive reactions		
	Step 1: nth order with autocatalysis		
	(w=0.250, n=0.64±0.50, ln k_{cat}=−0.266)	111.8±6.2	17.3±1.4
	Step 2: nth order		
	(w=0.750, n=0.276±0.044)	111.1±0.6	15.25±0.13

Table 7
Set 7: (see also Fig. 7) five simulated alpha-temperature curves calculated at heating rates of 0.5, 1.0, 2.0, 4.0 and 8.0 K min^{-1}, FILE: SIMKPM.TXT

Contributor	Method	E_a/kJ mol^{-1}	ln (A/s^{-1})
Anderson	TA-KIN for Windows 1.6		
	Reaction order n=1.5	100.4	25.09
	Avrami n=0.75	104.4	26.03
Burnham	Friedman n=1		
	Low α=0.1	87.7±0.6	20.86
	High α=0.9	117.3±1.7	29.62
	Coats-Redfern (modified)		
	Low α=0.1	85.2±0.4	20.08
	High α=0.9	117.3±1.7	27.85
	First-order (Kissinger)	96.3±0.3	23.57
	Concurrent nth order NLR		
	Step 1: n=1.0002; w=0.4998	80.08	18.93
	Step 1: n=1.0003; w=0.5002	120.11	30.44

Table 7 (*Continued*)

| Contributor	Method	E_a/kJ mol^{-1}	ln (A/s^{-1})
Nomen and Sempere	Non-parametric method		
	Parallel first-order $w=0.50$		
	Step 1	79.8	18.52
	Step 2	120.4	30.55
Opfermann	Friedman		
	Low α	83.3±0.3	23.54
	High α	116.3±2.6	33.83
	Flynn, Wall, Ozawa		
	Low α	82.3±0.2	19.71
	High α	113.4±1.5	28.67
	ASTM E698	102.8±2.0	25.54
	Multivar-NLR		
	nth order: $n=1.291±0.024$	97.1±0.7	23.95±0.23
	Concurrent reactions		
	Step 1: $n=1$, $w=0.481$	79.54±0.07	18.79±0.02
	Step 2: $n=1$, $w=0.519$	118.96±0.05	30.10±0.02
	Consecutive reactions		
	Step 1: $n=1$, $w=0.533$	88.1±0.2	21.72±0.06
	Step 2: $n=1$, $w=0.467$	120.9±0.7	30.79±0.22
Roduit	Friedman		
	$\alpha=0.1$	89.2±1.7	
	$\alpha=0.9$	117.3±4.6	
	Flynn, Wall, Ozawa		
	$\alpha=0.1$	83.7±1.3	
	$\alpha=0.9$	106.7±2.7	
	ASTM	95.2±4.8	
	Multivar-NLR		
	Parallel first-order reactions		
	$w=0.499$	80.06±0.03	18.93±0.01
	$w=0.501$	120.04±0.04	30.42±0.01
Li and Tang	Flynn, Wall, Ozawa		
	Kissinger, Akahira and Sunrose		
	Li and Tang		
	All gave from low α to high α	85–115	
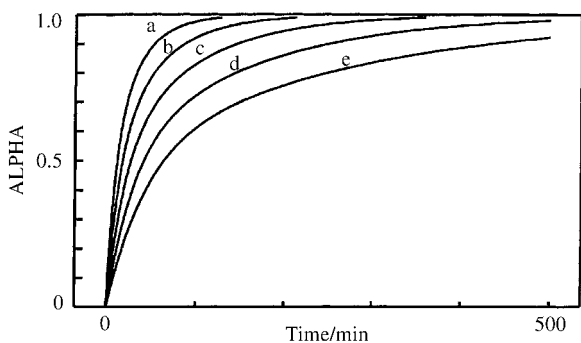
Fig. 8. Five simulated isothermal alpha-time curves calculated at temperatures of $a=380$, $b=375$, $c=370$, $d=365$ and $e=360$ K.

The Arrhenius parameters of the individual steps were taken to be $A_1=10^{10}$ min^{-1}, $E_1=80$ kJ mol^{-1}; $A_2=10^{15}$ min^{-1}, $E_2=120$ kJ mol^{-1}.

The kinetic results produced from data sets 1–4 are discussed by Maciejewski in Part B and for data sets 5–8 by Vyazovkin in Part C.

3. Kinetic parameters

As discussed in Section 1, the mathematical description of the data involves determining at least one kinetic triplet of parameters. The standard set of

Table 8

Set 8: (see also Fig. 8) five simulated isothermal alpha-time curves calculated at temperatures of a=380, b=375, c=370, d=365 and e=360 K, FILE: SIMISO.TXT

Contributor	Method	E_a/kJ mol^{-1}	ln (A/s^{-1})
Anderson	TA-KIN for Windows 1.6		
	Avrami n=0.75	101.2	24.97
Burnham	Friedman n=1		
	Low α=0.1	88.3±0.3	21.13
	High α=0.9	129.4±0.2	31.62
	Concurrent first-order		
	Step 1: n=1, w=0.502	80.13	18.94
	Step 2: n=1, w=0.498	120.26	30.49
Opfermann	Multivar-NLR		
	nth order: n=1.512	99.3±0.9	24.71±0.27
	Concurrent first-order		
	Step 1: n=1, w=0.502	80.133±0.007	18.948±0.002
	Step 2: n=1, w=0.498	120.275±0.004	30.495±0.001
	Consecutive first-order		
	Step 1: n=1, w=0.597	89.04±0.16	21.88±0.05
	Step 2: n=1, w=0.403	128.57±0.19	33.22±0.06
Roduit	Multivar-NLR		
	Parallel first-order reactions		
	w=0.506	79.94±0.03	18.93±0.01
	w=0.494	120.04±0.04	30.42±0.01
Set 7+Set 8			
Burnham	Friedman n=1		
	Low α=0.1	87.9±0.3	20.95
	High α=0.9	129.4±0.2	30.51
	Concurrent first-order		
	Step 1: n=1, w=0.501	80.06	18.92
	Step 2: n=1, w=0.499	120.35	30.51
Opfermann	Multivar-NLR		
	n-dim Avrami: n=0.822	101.3±0.6	25.06±0.18
	Concurrent first-order		
	Step 1: n=1, w=0.495	79.76±0.06	18.84±0.02
	Step 2: n=1, w=0.505	120.06±0.06	30.42±0.02
	Concurrent nth-order		
	Step 1: n=1.015±0.003, w=0.4995 79.7±0.1	79.7±0.1	18.82±0.03
	Step 2: n=1.010±0.003, w=0.5005	120.6±0.2	30.60±0.05
	Consecutive nth-order		
	Step 1: n=0.974±0.016, w=0.5319	88.1±0.2	21.72±0.07
	Step 2: n=1.093±0.017, w=0.4681	120.2±0.8	30.64±0.24
Malek and Mitsuhashi	Parallel first-order		
	$\alpha \to 0$	80	
	$\alpha \to 1$	120	

reaction models is well known [2,6]. The majority of the models can be accommodated in modifications of the Sestak–Berggren equation [7,8] which has the general form

$$\frac{d\alpha}{dt} = k(\alpha)^m (1 - \alpha)^n [-\ln(1 - \alpha)]^p$$

where n, m and p are constants. For m=p=0, this equation reduces to the common nth-order rate

equation. Often, p alone is set to zero, giving

$$\frac{d\alpha}{dt} = k(\alpha)^m(1-\alpha)^n$$

(Nomen and Sempere). For $m=n=1$ and $p=0$, the equation reduces to that of Prout and Tompkins [9] based on a model of nucleation and growth. It is necessary to assume an initial small value of α (produced through some initial process) for reaction to begin. To avoid the zero initial rate, Burnham and Braun [10] introduced a parameter q, which is ordinarily set to 0.99 but is user selectable

$$\frac{d\alpha}{dt} = k(1 - q(1-\alpha))^m(1-\alpha)^n$$

(Burnham). For $m=0$, $n=1$ and various values of p, the rate equations are those of the more generalised nucleation and growth models of Johnson–Mehl–Avrami–Erofeev [2,6].

$$\frac{d\alpha}{dt} = k(1-\alpha)[-\ln(1-\alpha)]^p$$

This is similar to what is commonly called the n-dimensional Avrami equation (Opfermann, Roduit).

$$\frac{d\alpha}{dt} = kn(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n}$$

The use of n as a general exponent in different reaction models can lead to some confusion.

4. Outline of the kinetic methods used

The isoconversional method of Flynn, Wall and Ozawa [11,13] (Tang, Opfermann, Desseyn, Roduit) is a 'model-free' method which involves measuring the temperatures corresponding to fixed values of α from experiments at different heating rates, β, and plotting $\ln(\alpha)$ against $1/T$

$$\ln(\beta) = \ln\left[A\frac{f(\alpha)}{(d\alpha/dT)}\right] - \frac{E_a}{RT}$$

and the slopes of such plots give $-E_a/R$. If E_a varies with α, the results should be interpreted in terms of multi-step reaction mechanisms [10,13]. This method is also referred to as ASTM E698 (Opfermann, Roduit).

The Kissinger [14,15] method (Li and Tang, Burnham) is to plot $\ln(\beta/T^2_{max})$ against $1/T_{max}$ for a

series of experiments at different heating rates, β_i. The slope of such a plot is $-E_a/R$. The method is a special case of determining A and E_a at a fixed conversion.

The method of Li and Tang [16,17] involves plotting $1/T$ against α and $\ln(d\alpha/dt)$ against α and for different heating rates. These plots are then numerically integrated to fixed α values and the integrals of $\ln(d\alpha/dt)$ are plotted against the integrals of $1/T$ for the set of heating rates used. The slopes of these plots give $-E_a/R$ and variations of E_a with T or with α are readily revealed. The value of E_a can be used to determine the kinetic model. No assumption needs to be made regarding the functional form of $f(\alpha)$.

The Kofstad method [18] (Desseyn) is based on a reaction order (RO) model ($f(\alpha)=(1-\alpha)^n$) written in the form

$$\ln\left\{-d\frac{[(1-\alpha)]}{dT}\right\} + (1-n)\ln(1-\alpha)$$
$$= \ln\left(\frac{A}{\beta}\right) - \frac{E_a}{RT}$$

For a number of (α, T)-values from one non-isothermal experiment, and after optimisation of the n-value, the left side of the equation may be calculated and plotted versus $1/T$, and the activation energy is calculated from the slope of the resulting line. The criterion used for the optimisation of the n-value is the correlation coefficient calculated for the straight line. The activation energy may be calculated as a function of alfa by taking (α, T)-values from only a part of the process.

The method of Ingraham and Marrier [19] (Desseyn) is similar, except that A is assumed to be a linear function of the temperature ($a=A'\cdot T$). No restriction was placed on the value of n, in contrast with the original method [19]. The equation used is

$$\ln\left\{\frac{\beta}{T}\frac{d\alpha}{dT}\right\} - n\ln(1-\alpha) = \ln(A') - \frac{E_a}{RT}$$

and the calculations are similar to the Kofstad method.

The isoconversional method of Friedman [20] (Desseyn, Opfermann, Burnham, Roduit) is based on equation

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left(\beta\frac{d\alpha}{dT}\right) = \ln A + \ln[f(\alpha)] - \frac{E_a}{RT}$$

which holds for an arbitrary reaction model, or on the equation

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left(\beta\frac{d\alpha}{dT}\right) = \ln A + n\ln(1-\alpha) - \frac{E_a}{RT}$$

which holds for a RO model. By plotting $\ln(d\alpha/dt)_i$ against $1/T_i$, one directly obtains $-E_a/R$ for a given value of α. This is a model-free method that can be applied to data sets obtained at different heating rates β_i and/or different temperatures, T_i. A value for A is obtained by extrapolation of a plot of the intercept against α_i to $\alpha_i=0$. In his original analysis, Friedman considered only the possibility that there was a single nth-order reaction present. If the value of E_a varies with extent of conversion, the results should be interpreted in terms of multi-step reaction mechanisms [9,12]

The Modified Coats-Redfern method (Burnham) [10,21] is a multi-heating rate application of the Coats and Redfern equation [18], producing a model-free isoconversional approach similar to those of Friedman and of Flynn, Wall and Ozawa. Using

$$\ln\left[\frac{\beta}{T^2(1-2RT/E_a)}\right]$$
$$= -\frac{E_a}{RT} + \ln\left(-\frac{AR}{E_a\ln(1-\alpha)}\right)$$

at fixed conversions for each of the heating rates, the left-hand side for each heating rate is plotted versus $1/T$ at that heating rate, giving a family of straight lines of slope $-E_a/R$, which is substituted into the intercept to obtain A. Since the left-hand side is a weak function of E_a, the process must be done iteratively by first assuming a value of E_a, then recalculating the left-hand side until convergence occurs. This is slightly more accurate than moving $(1-2RT/E_a)$ into the intercept and assuming it is a constant. If the value of E_a varies with extent of conversion, the results should be interpreted in terms of multi-step reaction mechanisms [10,13].

In the 'general method' (Desseyn), $f(\alpha)$ is incorporated in the intercept

$$\ln\left(\frac{d\alpha}{dT}\right) = \ln\left(\frac{Af(\alpha)}{\beta}\right) - \frac{E_a}{RT}$$

From a number of (α, T)-values from one non-isothermal experiment, the left side of the equation may be calculated and plotted versus $1/T$.

The isothermal method (Desseyn) involves writing the reaction rate at a certain constant temperature T as

$$\left(\frac{d\alpha}{dt}\right)_T = f(\alpha)\exp\left(-\frac{E_a}{RT}\right)$$

which, for a RO model, can be written as:

$$\ln\left[\frac{(d\alpha/dt)_T}{(1-\alpha)^n}\right] = \ln A - \frac{E_a}{RT}$$

From isothermal experiments at several different temperatures, rates are measured at constant α-values and the left-hand side of the above equation is plotted against $1/T$. The choice of the n-value only influences the value of the intercept, but not the value of the activation energy.

The Freeman and Carroll [22,23] method (Desseyn) assumes $f(\alpha)=(1-\alpha)^n$ and considers incremental differences in $(d\alpha/dT)$, $(1-\alpha)$ and $(1/T)$ which leads to the expression

$$\Delta\ln\left(\frac{d\alpha}{dT}\right) = n\Delta\ln(1-\alpha) - \left(\frac{E_a}{RT}\right)\Delta\left(\frac{1}{T}\right)$$

This expression can be used to determine the value of E_a by plotting

$$\left[\frac{\Delta\ln(d\alpha/dT)}{\Delta\ln(1-\alpha)}\right] \quad \text{against} \quad \left[\frac{\Delta(1/T)}{\Delta\ln(1-\alpha)}\right]$$

The intercept gives the reaction order, n. E_a can be calculated from the slope. The A value may be determined as a function of α by using the general equation with the calculated E_a and n values

$$\ln\left(\frac{d\alpha}{dT}\right) = \ln\left(\frac{A}{\beta}\right) + n\ln(1-\alpha) - \frac{E_a}{RT}$$

or

$$\ln\left(\frac{A}{\beta}\right) = \ln\left(\frac{d\alpha}{dT}\right) - n\ln(1-\alpha) + \frac{E_a}{RT}$$

The method of Malek and Mitsuhashi [24–27] required the use of differential data which were calculated using finite differences and $\Delta t=\Delta T/\beta$, where β is the heating rate. The apparent activation energy was calculated using an isoconversional method

$$\left[\text{dln}\frac{(d\alpha/dt)}{d(1/T)}\right]_\alpha = -\frac{E_a}{R}$$

The kinetic model can be determined by means of the

functions $y(\alpha)$ and $z(\alpha)$, defined under non-isothermal conditions by

$$y(\alpha) = \left(\frac{d\alpha}{dT}\right)\exp\left(\frac{E_a}{RT}\right) \quad \text{and} \quad z(\alpha) = \left(\frac{d\alpha}{dt}\right)T^2$$

and under isothermal conditions as

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right) \quad \text{and} \quad z(\alpha) = \left(\frac{d\alpha}{dt}\right)t$$

The value of E_a used above was taken as an average in the $0.3 \leq \alpha \leq 0.7$ range.

The 'non-parametric kinetics (NPK)' method [28,29] of Nomen and Sempere is based on the usual assumption that the reaction rate can be expressed as a product of two independent functions, $f(\alpha)$ and $f'(T)$. The reaction model $f(\alpha)$ accounts for the kinetic model and $f'(T)$ accounts for the temperature dependence, which need not be of the Arrhenius-type. The reaction rates, $d\alpha/dt$, measured from several experiments at different heating-rates, β, are organised as an $n \times m$ matrix whose rows correspond to different degrees of conversion, from α_1 to α_n, and whose columns correspond to different temperatures, from T_1 to T_m. The element i, j of matrix A is then $A_{i,j} = f(\alpha)_i f'(T_j)$. The functions $f(\alpha)$ and $f'(T)$ can then be discretised and expressed as column vectors, named $\boldsymbol{a}$ and $\boldsymbol{b}$, respectively, whose elements are the discretised values of the functions $f(\alpha)$ and $f'(T)$

$$\boldsymbol{a} = \{f(\alpha_1)f(\alpha_2)\ldots\ldots f(\alpha_n)\}^T$$
$$\boldsymbol{b} = \{f'(T_1)f'(T_2)\ldots\ldots f'(T_m)\}^T$$

The reaction rate can then be expressed in the form of a matrix product

$$A = \boldsymbol{a}\,\boldsymbol{b}^T$$

The NPK method uses the singular value decomposition (SVD) algorithm [30] to decompose matrix A into the two vectors $\boldsymbol{a}$ and $\boldsymbol{b}$. These vectors can then be further analysed by examining the resulting plots of rate against α (to determine the kinetic model) and of rate against temperature (to check on Arrhenius-type behaviour and to determine Arrhenius parameters when appropriate). The NPK method uses a large number of points and a wide range of temperatures. This is a model-free method in the sense that it allows for isolating the temperature dependence of the reaction rate (and, therefore, the activation energy)

without making any assumptions about the reaction model.

Some participants did kinetic analyses on the combined dynamic and isothermal sets for the same compound under the same conditions.[1]

5. Description of software packages

5.1. TA-KIN for windows v1.6 (Anderson) [31–33]

The evaluation of the delivered data sets has been performed on the basis of the well known and acknowledged models of chemical kinetics. The temperature dependence of the rate constant is of Arrhenius type. The evaluation itself has been performed using the non-linear optimisation algorithm of Levenberg and Marquardt. For the numeric integration of the differential rate laws the method of Runge–Kutta–Fehlberg has been used. So it was possible to evaluate the unchanged data sets. The method does not use numerical differentiation or linearisation which may lead to erroneous results subject to significant experimental noise. To avoid any simplifications and approximations, the kinetic rate laws have been used in the form of differential equations.

5.2. NETZSCH thermokinetics software (Opfermann)

Details of these programs are given in references [34,35].

5.3. KINETICS for Windows 95/98/NT (Burnham) [10]

Kinetics for Windows 95/98/NT uses various simple linear regression methods to determine initial

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[1] Summary of methods of kinetic analysis used by the contributors; Flynn, Wall and Ozawa (Tang, Opfermann, Desseyn, Roduit); ASTM E698 (Opfermann, Roduit); Kissinger, Akahira and Sunrose (Tang); Li and Tang (Tang); Kofstad (Desseyn); Ingraham and Marrier (Desseyn); Friedman (Desseyn, Opfermann, Burnham, Roduit); Freeman and Carroll (Desseyn); Modified Coats-Redfern (Burnham); 'general' (Desseyn); Non-parametric method (Nomen and Sempere); Distributed reactivity models (Burnham); Malek and Mitsuhashi; Direct non-linear optimisation on the basis of unchanged data sets [24,35,36]; Multivariable non-linear regression NLR (Burnham, Opfermann, Roduit).

guesses for non-linear regression of a variety of kinetic models. All the linear regression methods are variations of isoconversional methods, including the Friedman method, a multi-heating-rate Coats–Redfern method, and several extensions of the Kissinger method. The Friedman method applies to any thermal history, while the last two methods apply only to constant heating rate data. For the extended Kissinger methods, correlations involving profile width and asymmetry relative to those of a first-order reaction are used to estimate reaction order, nucleation order, or Gaussian activation energy distribution, as appropriate. The non-linear regression models include up to three parallel nth-order reactions (including $n=1$), three parallel Sestak–Berggren reactions, three parallel distributed activation energy reactions for which the activation energy distribution can be Gaussian or Weibull, consecutive nth-order Gaussian reactions, and an arbitrary discrete distribution of parallel first-order reactions having either the same A or $A=a+bE_a$. The program is available for US Government use (Kinetics98) through the Energy Science and Technology Software Center, Oak Ridge, TN, and for commercial use (Kinetics2000) through Humble Instruments and Services, Humble, TX.

5.4. AKTS-TA for Windows 95–98/NT (Roduit)

AKTS-TA Software provides for both model-fitting and model-free kinetic analysis (Friedman, Ozawa–Flynn–Wall, ASTM) of solid state reactions occurring under isothermal or non-isothermal conditions. It determines the best kinetic schemes, Arrhenius parameters, kinetic models and their contributions from among 22 models specified in the literature. Due to the multi-step nature of the solid state reactions, an appropriate statistical criterion determines the eventual necessity of introducing additional models. The prediction of the course of the investigated reaction under different heating rates (non-isothermal mode) or different temperatures (isothermal mode) is straightforward after determination of the kinetic parameters. Input of the data from different instruments can be achieved using ASCII files. AKTS-TA Software runs under Windows 95/98 and Windows NT. It is available for commercial use through AKTS Corp., Charlotte (NC), USA.

6. Results

The kinetic parameters (the reaction model (or kinetic model), the activation energy (E_a/kJ mol^{-1}) and the Arrhenius pre-exponential factor (A/s^{-1})) have been collected, from the detailed analyses provided, for each data set. These parameters are listed in tables numbered according to the original data set. Comparison of pre-exponential factors is sometimes not straightforward because of uncertainty regarding units and accumulation of terms in what is often the intercept of linear regression.

7. Discussion and conclusions

Parts B and C of this series of papers present detailed individual discussions, by two of the organizers (Maciejewski and Vyazovkin, respectively) of the Project, of the kinetic results described in Part A. Parts D and E are individual points-of-view provided by two of the participants in response to an invitation to all participants.

In this section, some general tendencies in kinetic analysis that were noted, are summarised. As mentioned in Section 1, the ability to handle multi-step reaction mechanisms is a desirable feature of a computational method. Multi-heating rate and isoconversional methods have proven to be particularly effective and most of the recent interest in the field of kinetic computations has been concerned with these methods. This interest is likely to continue into the next millennium. Reasonably consistent kinetic results were obtained for isothermal and non-isothermal data.

This Project has demonstrated that there is ample computational machinery available for testing the 'goodness-of-fit' of experimental data to the limited set of kinetic equations. However, the goodness of fit is only the necessary, but not the sufficient condition for the identified reaction model to be physically sound. Extreme care has to be exercised that the introduction of additional kinetic parameters can be justified by physical significance, and not only by improvement of the goodness of fit.

There is an unfortunate implication that methods of kinetic analysis are in *competition* with each other. Provided that the methods are computationally sound,

they should rather be seen as *complementary*, providing increased confidence in the resulting parameters. It is a considerable advantage to remove the influence of the kinetic model from the kinetic analysis while estimating the Arrhenius parameters, but a full kinetic analysis should consider the problems of identification of the function or functions (however complex these may turn out to be [36]) which determine the extent of reactant conversion.

There is also a need for a shift of emphasis from computational aspects of kinetic analysis (Stage 2) to better planning of experiments to reveal details of the important bond redistribution processes leading to new compounds and/or new structures (Stage 1) and the difficulties of interpretation of results (Stage 3). There is an obvious need for investigations into the reaction mechanisms of multi-step solid-state processes. Future studies need to be chosen to probe particular factors which may control solid state reactions. For example, studies on selected series of coordination compounds should, in principle, allow some factors (perhaps structure?) to be held constant while varying others (ligand?) to test the influences on stability as measured by the kinetic parameters. On the other hand, various physical processes such as melting [37], sublimation, diffusion, adsorption, sintering, crystallisation, etc. may also control the overall reaction kinetics. The effect of these factors on kinetic parameters also needs to be thoroughly addressed.

8. Nomenclature

α	fractional reaction
β	heating rate
t	time
T	temperature
A	Arrhenius pre-exponential factor (assumed to have units of s^{-1})
E_a	Arrhenius activation energy (kJ mol^{-1})
n	order of reaction; (sometimes more generally as the single exponent in a reaction model)
m	exponent of α in the Sestak–Berggren equation
p	exponent of $[-\ln(1-\alpha)]$ in the Sestak–Berggren equation
w	weighting factor in complex reactions
$f(\alpha)$	differential reaction model
$g(\alpha)$	integral reaction model
$y(\alpha)$	see Malek and Mitsuhashi above
$z(\alpha)$	see Malek and Mitsuhashi above
A	reaction rate matrix
a	vector related to temperature dependence
b	vector related to degree of conversion dependence

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