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Influence of experimental conditions on the kinetic parameters of gas–solid reactions —parametric sensitivity of thermal analysis[1]

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Abstract

The influence of experimental conditions on the kinetic parameters of gas–solid reactions has been investigated using the reduction of nickel oxide by hydrogen as a model reaction. The experimental parameters studied were heating rate, sample mass, total gas flow and hydrogen concentration.

For arbitrarily chosen "standard conditions" the kinetic parameters best describing the course of the reaction were calculated using the global curves analysis method. Experiments were carried out with different heating rates, in the range 1.3–10.6 K min^{-1}. Twenty two kinetic models of solid-state reactions proposed in the literature were tested using numeric integration methods.

The confidence space, in which the kinetic parameters, calculated for "standard conditions", fit the kinetics of NiO reduction properly, was calculated taking into account the influence of all investigated variables.

The results illustrate the great influence of the experimental conditions on the measured thermoanalytic curves ("parametric sensitivity") and demonstrate the limited validity of kinetic data calculated from experiments carried out under arbitrary chosen conditions.

Keywords: Influence of experimental conditions; Kinetic parameters; NiO reduction

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List of symbols

a	constant in Eq. (10)	(–)
A	preexponential factor in Arrhenius equation	(s^{-1})

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[1] Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

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α	reaction progress	(–)
b	constant in Eq. (10)	(–)
β	heating rate	(K min^{-1})
C	hydrogen concentration	(vol%)
$\bar{C}$	average hydrogen concentration over the crucible	(vol%)
d	parameter of the F-distribution	(–)
Δ	interval	(–)
E	activation energy in Arrhenius equation	(kJ mol^{-1})
F	approximated formula of the F-distribution	(–)
$f(\alpha)$	model of solid state reaction — differential forms of kinetic functions	(–)
f_1	degrees of freedom of the F-distribution (standard conditions)	(–)
f_2	degrees of freedom of the F-distribution (changed conditions)	(–)
h	parameters of the F-distribution	(–)
M	number of heating rates	(–)
n	reaction order in the $f(\alpha)$ function	(–)
N	number of experimental points for one thermogram	(–)
P	probability	(–)
Q	number of parameters of the experiment	(–)
r	correlation coefficient for Eq. (10)	(–)
R	gas constant 8.314 kJ mol^{-1}	(kJ mol^{-1})
RSS	residual sum of squares between experimental and calculated values	(–)
S	sample mass	(μmol)
t	time	($\text{m}^3\,\text{s}^{-1}$)
T	temperature	(K)
u_P	value of the standard normal distribution for P, f_1 and f_2	(–)
V	total gas flow rate	(mL min^{-1})
W	sample weight	(mg)
z	help function for the F-distribution	(–)

Subscripts

cal	calculated value
exp	experimental value
i	i^{th} value
j	j^{th} value
l	lower limit
out	final value
Std	standard conditions
u	upper limit
W	reasonable from experimental point of view

X	to determine a type of model
X′	to determine another type of model

1. Introduction

It has often been reported in the literature that the kinetic parameters of solid–gas reactions, i.e. activation energy, *E*, pre-exponential factor, *A*, and the function of the reaction extent, $f(\alpha)$, depend on the experimental conditions and that it is difficult to accept them as intrinsic constants of the investigated reaction [1–7]. Many papers illustrate this problem and present the influence of sample weight [8–19], atmosphere [11, 20, 23–33], gas flow [11, 12, 20–22], or crystallite size [12, 20, 34–36], on the course of the kinetic curves measured for decomposition of solids or reactions of solids with a gas (oxidation, reduction). In several of the above cited studies one can find empirical relationships between, e.g., sample mass and activation energy in the form of polynomial expressions, which were calculated assuming that the mechanism of the process remains unchanged under different conditions. This simple assumption is often not valid, as shown, e.g., in a previous paper [37] dealing with $CaCO_3$ decomposition under different atmospheres. Regarding the influence of the decomposition atmosphere (vacuum, nitrogen or carbon dioxide) not only *E* and *A*, but also the shape of the thermogravimetric curves has varied, indicating a change of the form of the $f(\alpha)$ function dependent on the kinetic models of the solid-state reactions.

The calculation of the kinetic parameters for a given reaction is usually performed on the basis of data obtained under certain experimental conditions, such as arbitrarily chosen sample mass, gas flow, gas composition, heating rate (non-iso-) or temperature (isothermal mode). These variables are bound to different ranges depending on the thermoanalyser used, but generally they are in the ranges: sample weight 1–1000 mg, gas flow 10–500 mL min^{-1}, concentration of the reactive gas 1–100 vol%, heating rate 1–50 K min^{-1}. The *n*-dimensional space containing all *n* possible experimental conditions applied in conventional thermoanalytical experiments is thus well-defined, but often kinetic data are calculated only for one point of this space, determined by the set of conditions used.

If for simplification we consider only three experimental variables: the sample mass *S*, the flow rate of the gas *V*, and the concentration of the reactive gas *C* (e.g. hydrogen in NiO reduction) then the three-dimensional space (S, V, C) containing the possible experimental conditions can be represented as shown in Fig. 1. Kinetic parameters calculated from the data obtained under arbitrarily chosen experimental conditions, e.g. sample mass 50 mg, gas flow rate 50 mL min^{-1}, and hydrogen concentration 10 vol% (represented by point A in Fig. 1) are only valid strictly for this point or its vicinity in the three-dimensional space. A common mistake is the facile assumption that kinetic parameters calculated for the conditions represented by point A are characteristic for other experimental conditions lying in the space limited by the boundaries imposed by the experimental restrictions. This unjustified assumption can easily lead to different kinetic parameters being determined for the same reaction, and provokes several debates about their relevance. Clearly, the course of any reaction carried out under the

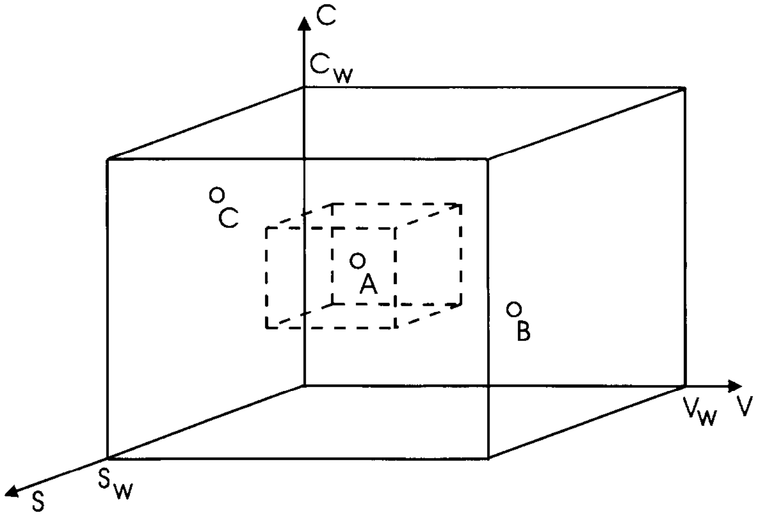

Fig. 1. Three-dimensional space (S, V, C) representing boundaries of possible changes of the experimental conditions. Dashed volume represents the "isokinetic" space in which the course of the reaction can be described by kinetic parameters calculated from the data obtained under conditions represented by point A.

conditions represented by point B (Fig. 1) will differ from that performed at point C; this in turn indicates that their kinetic parameters are not the same. Of course, for each compound and each reaction the parametric sensitivity of the thermal analysis (i.e. the influence of the change of the experimental parameters on the course of the investigated reaction) is different, e.g. the influence of the experimental conditions on the polymorphic transformation of a solid is less significant than for its reversible decomposition.

The aim of the present paper is to describe the parametric sensitivity quantitatively, using as a model reaction the reduction of NiO by hydrogen. The intention was to find the spatial domain where reactions carried out under various experimental conditions can be described by the same set of kinetic parameters. In other words, going from the kinetic description for arbitrarily chosen "standard conditions" represented by point A (Fig. 1), we describe the boundaries within which the experimental conditions can be changed without affecting the estimated values of the kinetic parameters ("isokinetic space"; space represented in Fig. 1 by the dashed domain).

2. Experimental and methods of calculation

The NiO used for the experiments was prepared by decomposing nickel nitrate hexahydrate for 15 h at 400°C. The reduction experiments were performed on a Netzsch STA 409 thermoanalyser coupled by a heated capillary to a Balzers QMG 420 quadrupole mass spectrometer. X-ray powder diffraction of the product showed only patterns of NiO (JCPDS file 4-850) and mass spectrometry confirmed the total decomposition of the reactant (no residual NO_3^-). The weight loss measured during reduction of the NiO by hydrogen (21.3 wt%) agreed well with the stoichiometric value of 21.42 wt%.

The experimental parameters were changed in the following ranges:

(1) sample weight	S:	7.47–37.35 mg, i.e. 100–500 μmol.
(2) total gas flow	V:	30–120 mL (STP) min^{-1}
(3) hydrogen concentration	C:	3–25 vol%, balance: argon
(4) heating rate	β:	1.3–10.6 K min^{-1}

The kinetic analysis of the thermogravimetric curves (TG) was based on the assumption that the reaction rate can be described by an Arrhenius-type temperature-dependence ($A \exp(-E/RT)$) in the various kinetic models of the solid-state reactions corresponding to different $f(\alpha)$ functions. A list of the various forms of $f(\alpha)$ used is presented in Table 1. Additionally, as previously applied by Monti and Baiker [38] in the investigation of the parametric sensitivity of temperature-programmed reduction

Table 1
Different forms of kinetic functions $f(\alpha)$

Kinetic model	Symbol	$f(\alpha)$
Power law	Pn	$n\alpha^{(1-1/n)}$
	P1	α^0
	P2	$2\alpha^{1/2}$
	P3	$3\alpha^{2/3}$
	P4	$4\alpha^{3/4}$
Nucleation and nuclei growth		
Random nucleation (Mampel model)	F1,(A1)	$1-\alpha$
Avrami–Erofeev nuclei growth	An	$n(1-\alpha)[-\ln(1-\alpha)]^{(1-1/n)}$
	A1.5	$1.5(1-\alpha)[-\ln(1-\alpha)]^{1/3}$
	A2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$
	A3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$
	A4	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$
Diffusion		
Parabolic law, one-dimensional diffusion	D1	$1/(2\alpha)$
Valesi, two-dimensional diffusion	D2	$[-\ln(1-\alpha)]^{-1}$
Jander, three-dimensional diffusion, spherical symmetry	D3	$1.5[1-(1-\alpha)^{1/3}]^{-1}(1-\alpha)^{2/3}$
Ginstling–Brounshtein, three-dimensional diffusion	D4	$1.5[(1-\alpha)^{-1/3}-1]^{-1}$
Phase-boundary reaction	Rn	$n(1-\alpha)^{(1-1/n)}$
Two-dimensional movement (shrinking cylinder)	R2	$2(1-\alpha)^{1/2}$
Three-dimensional movement (shrinking sphere)	R3	$3(1-\alpha)^{2/3}$
n-Order reactions	Fn	$(1-\alpha)^n$
First order	F1	$1-\alpha$
Second order	F2	$(1-\alpha)^2$
Third order	F3	$(1-\alpha)^3$

(TPR), the material balance of hydrogen was taken into account. The extent of the reaction, α, is defined as

$$\alpha = \frac{W_0 - W}{W_0 - W_f} \tag{1}$$

where W_0, W and W_f represent initial mass, actual mass at temperature T, and final mass of NiO, respectively. The rate of the reaction is expressed by the commonly used equation

$$\frac{d\alpha}{dt} = A \exp(-E/RT) f(\alpha) \tag{2}$$

where A, E, R and T have their usual meaning.
A hydrogen balance over the thermoanalyser reaction space gives:

$$VC = VC_{out} + S\frac{d\alpha}{dt} \tag{3}$$

where:
V — total gas flow
C, C_{out} — hydrogen concentration at the inlet and outlet of the thermoanalytical oven
S — initial mass of solid sample
Assuming an average hydrogen concentration $\bar{C}$ over the crucible:

$$\bar{C} = \frac{C + C_{out}}{2} \tag{4}$$

the equation (Eq. (2)) describing the rate of the reduction changes to:

$$\frac{d\alpha}{dt} = A \exp(-E/RT)\bar{C} f(\alpha) \tag{5}$$

For a non-isothermal run performed with a heating rate β,
where

$$\beta = \frac{dT}{dt} \tag{6}$$

$$T = T_0 + \beta t \tag{7}$$

After elimination of the average hydrogen concentration in the reaction space using Eqs. (3) and (5) we obtain:

$$\frac{d\alpha}{dt} = \frac{2VC}{S\beta}\left(1 + \frac{2V}{SA\exp(-E/RT)f(\alpha)}\right) \tag{8}$$

which is used for the determination of the kinetic parameters as a function of the experimental conditions.

3. Results and discussion

3.1. The influence of the experimental conditions on the course of NiO reduction.

The influence of the change of the sample mass, total gas flow, hydrogen concentration and heating rate on the course of NiO reduction is presented in Figs. 2–5. The results obtained under arbitrarily chosen "standard conditions" i.e. $\beta = 5.5\,\mathrm{K\,min^{-1}}$, $S = 250\,\mu\mathrm{mol}$, $V = 50\,\mathrm{mL\,min^{-1}}$ and $C = 10\,\mathrm{vol\%}$ H_2 are represented in these figures by dashed lines. TG curves obtained under these conditions were used for calculation of the kinetic parameters using Eq. (8) and our computer program described elsewhere [39].

Eq. (8) cannot be solved analytically and requires numerical integration. The mathematical procedure applied involved the following steps: on the basis of the data taken from four experiments carried out with different heating rates, the activation energy E was calculated using the well-known iso-conversional Ozawa method [40]. Next, the linear regression method establishing the relationship $\ln((\mathrm{d}\alpha/\mathrm{d}t)/f(\alpha))$ vs. $(1/T)$ was performed for all functions $f(\alpha)$ presented in Table 1 with the reaction order n in $f(\alpha)$ kept as constant. Differentiation between all models $f(\alpha)$ was done by considering the similarity of the E values obtained from both methods (Ozawa: independent of any kinetic model; linear regression method: dependent on the applied kinetic model). Regarding the correlation coefficient of the linear regression, both methods enable discrimination between different functions $f(\alpha)$ showing a similar relationship α vs. T.

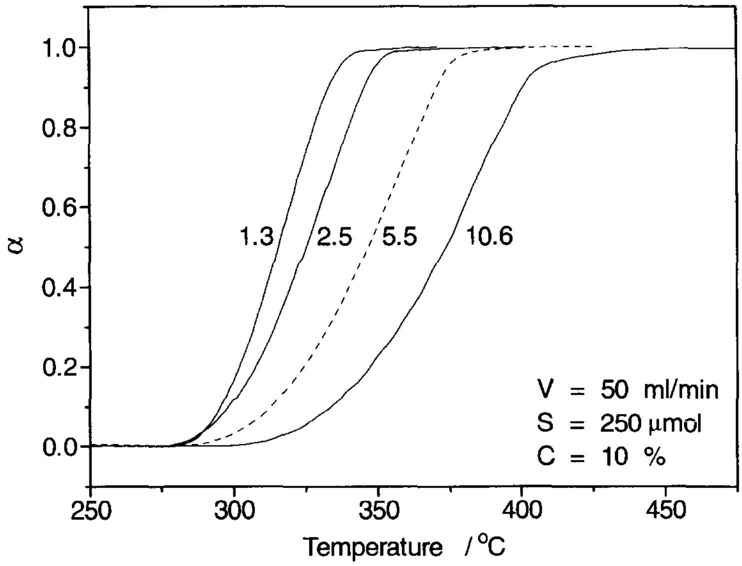

Fig. 2. Progress of NiO reduction as a function of the heating rates marked on the curves in K min^{-1}. Dashed curve represents the result obtained under "standard conditions" ($\beta = 5.5\,\mathrm{K\,min^{-1}}$; $S = 250\,\mu\mathrm{mol}$; $V = 50\,\mathrm{mL\,min^{-1}}$; C = 10% H_2).

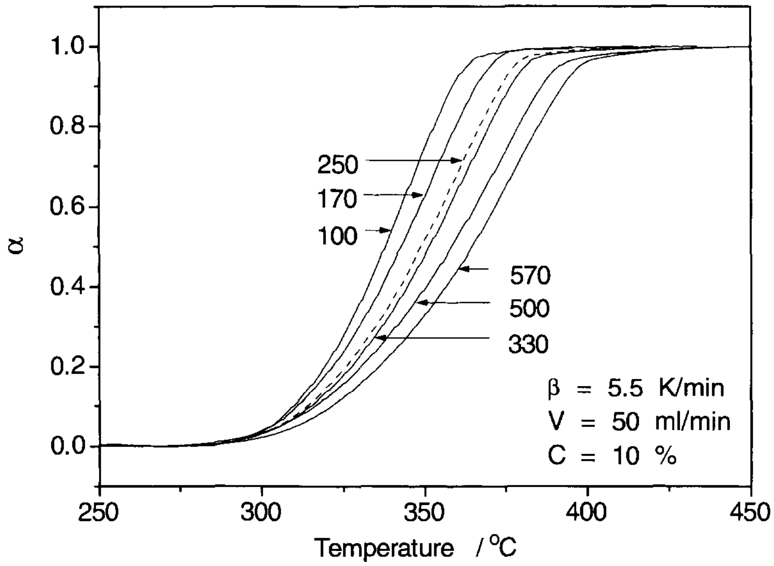

Fig. 3. Progress of NiO reduction as a function of the sample weight marked on the curves in μmol. Dashed curve — standard conditions.

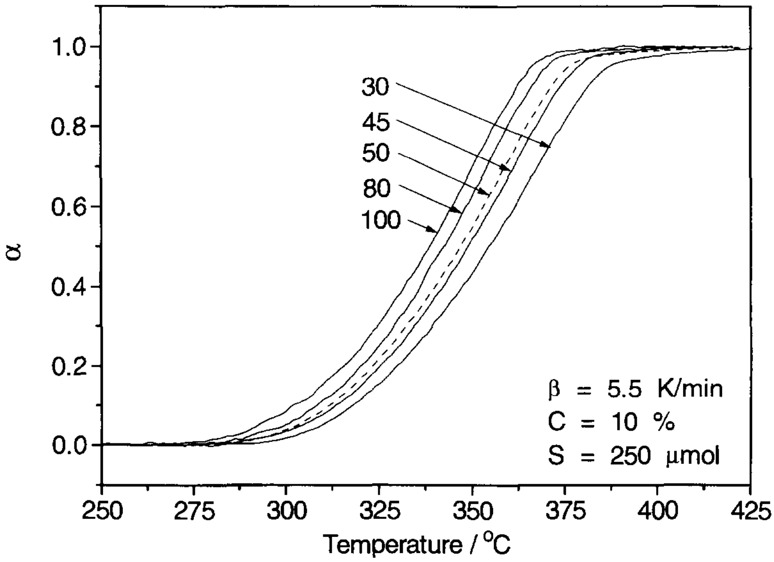

Fig. 4. Progress of NiO reduction as a function of the total gas flow marked on the curves in mL min^{-1}. Dashed curve — standard conditions.

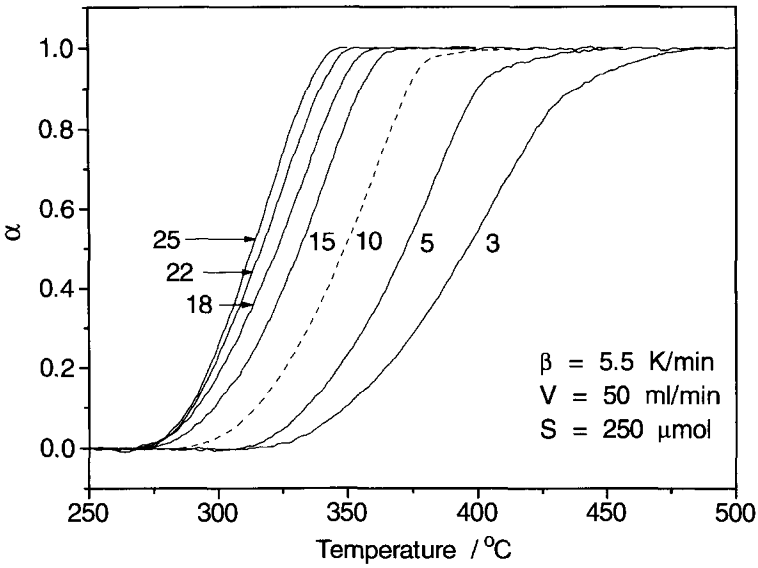

Fig. 5. Progress of NiO reduction as a function of H_2 concentration marked on the curves in vol%. Dashed curve — standard conditions.

The most suitable model of functions $f(\alpha)$ (Avrami–Erofeev in the present case) was then applied in Eq. (8), where for each experimental point the squared difference between the α value computed for that point and the experimental value was calculated. The optimization of the kinetic parameters was performed by minimizing the total residual sum of squares for the four heating rates.

$$\sum_{j=1}^{M} \sum_{i=1}^{N} (\alpha_{i,j}(\mathrm{exp}) - \alpha_{i,j}(\mathrm{cal}))^2 \tag{9}$$

($M = 4$: number of heating rates)

($N = 40$–60: number of experimental points for one thermogram)

The applied numerical integration procedure adjusts A, E and the reaction order n in the previously chosen $f(\alpha)$ function in Eq. (8). Using this procedure, the following kinetic parameters describing the NiO reduction under standard conditions were calculated on the basis of experiments carried out with the heating rates 1.3, 2.5, 5.5 and 10.6 K min^{-1}:

model	Avrami–Erofeev
$f(\alpha)$	$n(1-\alpha)[-\ln(1-\alpha)]^{1/n}$
E	84.0 kJ mol^{-1}
A	7.5e + 03 $\mathrm{m}^3\ \mathrm{mol}^{-1}\ \mathrm{s}$ (note unconventional A units resulting from introducing experimental variables S, V, and C into the rate equation)
n	1.47

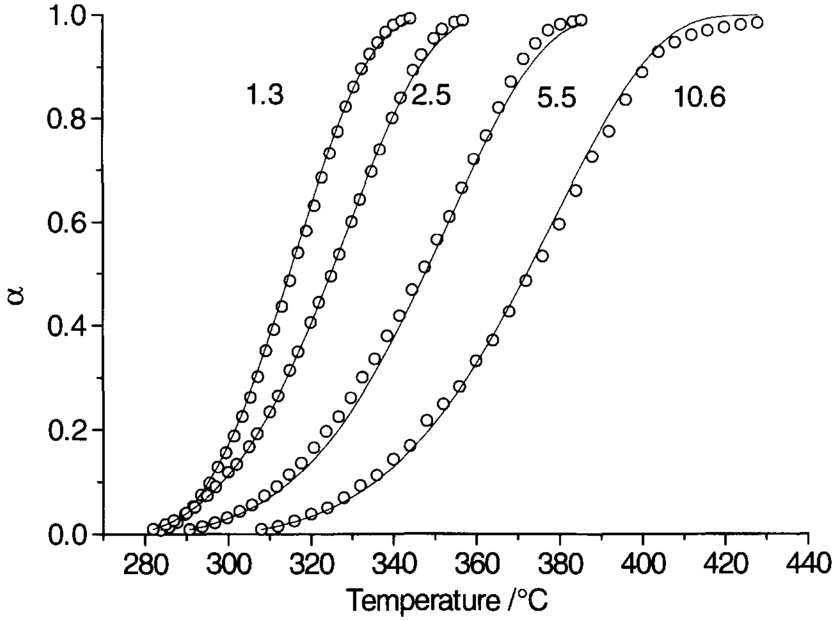

Fig. 6. Reaction extent, α, as a function of temperature for the reduction of NiO by hydrogen under the conditions: sample mass $S_{Std} = 250\,\mu$mol, gas flow rate $V_{Std} = 50$ mL min^{-1}, hydrogen concentration $C_{Std} = 10$ vol%, heating rates $\beta = 1.3; 2.5; 5.5; 10.9$ K min^{-1} (marked on the curves). Experimental data are presented as open circles, solid lines represent the relationships α–Tcalculated from the determined kinetic parameters.

Calculations were done for α values lying in the range $0.01 < \alpha < 0.99$. Comparison of the experimental data with the calculated curves obtained with the above kinetic parameters is presented in Fig. 6.

3.2. Influence of hydrogen concentration on kinetic parameters of NiO reduction by hydrogen

In order to examine the influence of the hydrogen concentration on the kinetics of the process (this experimental variable has the strongest effect on the course of the reduction (see Figs. 2–5)), we calculated the kinetic parameters for the reactions performed under different H_2 concentrations (varying in the range 3–25 vol%), keeping constant — as for standard conditions — the two other parameters. Results of these experiments performed for each H_2 concentration with at least four different heating rates are summarized in Table 2.

Irrespective of the hydrogen concentration, in all cases the reduction is described best by the Avrami–Erofeev model with exponent n varying in the range 1.17–1.64. This indicates that one of the kinetic parameters i.e. $f(\alpha)$ is the same in the investigated range of experimental conditions. In contrast, one observes a great change for two other

Table 2
Influence of the hydrogen concentration on the kinetic parameters (applied model: Avrami–Erofeev)

Hydrogen concentration C/vol%	$A/(\mathrm{m}^3\,\mathrm{mol}^{-1}\,\mathrm{s})$	$E/(\mathrm{kJ\,mol}^{-1})$	n
5	3.90e + 03	80	1.17
10	7.50e + 03	84	1.47
20	3.00e + 02	69	1.64
40	6.66e + 05	105	1.48
75	1.20e + 08	130	1.43

kinetic parameters: A and E — their mutual relationship is known in the literature as a "kinetic compensation effect" [41, 42]. Compensation constants in terms of the equation

$$\log(A\,\mathrm{mol\,s\,m}^{-3}) = a + (b\,\mathrm{mol\,kJ}^{-1})E \tag{10}$$

are (see also graphical presentation of this relationship in Fig. 7):
$a = -3.77 \pm 0.094$
$b = 0.0913 \pm 0.00098$
The correlation coefficient of the linear regression analysis is $r = 0.99983$. The presented results illustrate that even when the kinetic data are fitted by the same function under varying experimental conditions, a different set of A and E describes the kinetics of the process.

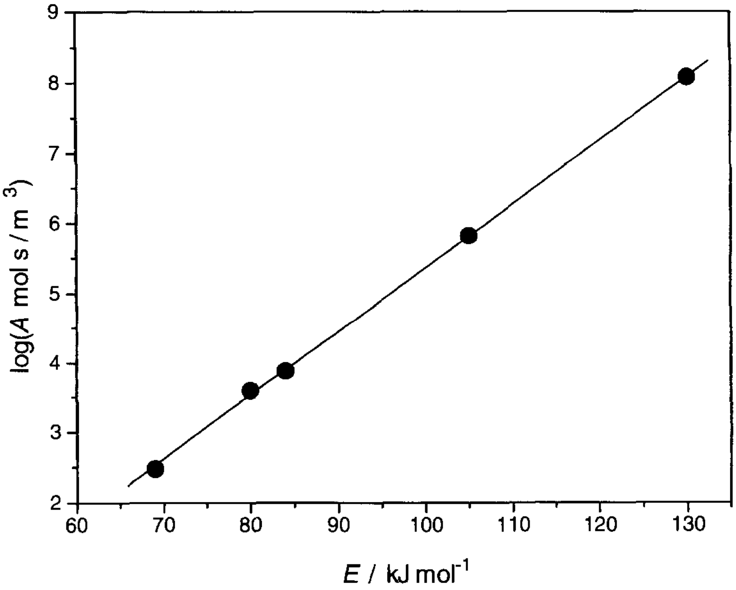

Fig. 7. Kinetic compensation effect in terms of the equation $\log(A\,\mathrm{mol\,s\,m}^{-3}) = a + (b\,\mathrm{mol\,kJ}^{-1})E$.

3.3. Determination of the range of validity of the kinetic parameters calculated under "standard conditions"

In order to find the mutual interdependence of all three experimental conditions (sample mass, total gas flow and hydrogen concentration) on the calculated kinetic parameters we used the statistical F-test. The F-distribution function is used for calculating confidence limits or ranges for each variable (S, V and C), in which A, E, $f(\alpha)$ and n (determined from experiments performed under "standard conditions") will describe with 95% probability (default) the data obtained under "standard conditions" as well as the data obtained if one of the experimental parameters is changed. By repeating this procedure for all three variables successively, we can determine the confidence space in which, for different reaction conditions, the reduction of NiO can be properly described by the kinetic parameters estimated for "standard conditions". This method enables quantification of the influence of the operating variables (S, V, C) and thereby the parametric sensitivity of the thermal analysis.

The F_{95}-test indicates with 95% probability that the model ($f(\alpha)_X$) with kinetic parameters (A_X, E_X, n_X in $f(\alpha)_X$) calculated from the data obtained under the conditions (S_X, V_X, C_X, (β_{X_1}, β_{X_2}, β_{X_3}, β_{X_4})) fits the corresponding experimental results as well as the data obtained under other conditions ($S_{X'}$, $V_{X'}$, $C_{X'}$, (β_{X_1}, β_{X_2}, β_{X_3}, β_{X_4})).

3.4. Determination of the F-distribution

To perform the F-test for the chosen confidence level, the F-distribution can, if $f_1 > 4$ and $f_2 > 5$, be approximated by Eq. (11) [43]

$$F(f_1 \approx 50, f_2 \approx 50, P = 0.95) = e^{2z(f_1, f_2, P)} \tag{11}$$

where:

f_j	N-Q, degrees of freedom of the F-distribution
subscript 1	standard experimental conditions with their kinetic parameters
subscript 2	new experimental conditions (S, V and C changed in sequence or together), but kinetic parameters taken as for the standard conditions.
N	number of the experimental points for one thermogram (40–60)
P	probability: 95%
Q	number of experimental parameters (7: V, C, S, β, A, E, n)

z in Eq. (11) is expressed by the formula:

$$\begin{aligned} z(f_1, f_2, P) = {} & \frac{u_p}{\sqrt{h}} - \frac{d}{6}(u_P^2 + 2) + \frac{1}{\sqrt{h}}\left[\frac{u_P^3 + 3\,u_P}{12h} + \frac{(u_P^3 + 11\,u_P)hd^2}{144}\right] \\ & - \frac{d}{60\,h}(u_P^4 + 9u_P^2 + 8) + \frac{hd^3}{6480}(3\,u_P^4 + 7u_P^2 - 16) \\ & + \frac{1}{h}\left[\frac{u_P^5 + 20\,u_P^3 + 15u_P}{480h^2} + \frac{(u_P^5 + 44u_P^3 + 183\,u_P)d^4}{2880}\right] \\ & + \frac{d^4h^2}{622080}(9u_P^5 - 284\,u_P^3 - 1513\,u_P) \end{aligned} \tag{12}$$

where:

$$d=\frac{1}{f_1}-\frac{1}{f_2} \quad \text{and} \quad h=\frac{2}{\frac{1}{f_1}+\frac{1}{f_2}}$$

The value of the standard normal distribution u_P for $P=95\%$ and $f_1 \approx 40$–60 and $f_2 \approx 40$–60 is equal to 1.6759.

In order to evaluate quantitatively the quality of fitting of the experimental data obtained under conditions different from the standard conditions by the kinetic parameters calculated for standard conditions, we applied the following expression:

$$F_{\mathrm{exp}}=\frac{RSS_2/f_2}{RSS_1/f_1}$$

with $RSS_1/f_1 > RSS_2/f_2$, where RSS_1/f_1 is the mean value derived from three experiments (in order to consider the influence of the experimental errors) performed under "standard conditions".

RSS is defined as follows:

$$RSS=\sum_{i=1}^{N}(\alpha_{\mathrm{exp},i}-\alpha_{\mathrm{cal},i})^2$$

A ratio F_{exp}/F greater than 1 indicates that the kinetic parameters determined for "standard conditions" do not properly describe new experimental data resulting from changing one (or more) experimental conditions.

3.5. Influence of experimental conditions on the statistical criterion characterizing the usefulness of the kinetic parameters obtained under "standard conditions" for the description of the data obtained by changing all the experimental variables (V, C, S, β).

As emerges from Figs. 3–5, the course of NiO reduction depends in different ways on changes of the particular experimental variables. In order to describe this relationship quantitatively, i.e. to express mathematically the parametric sensitivity of the thermal analysis, we performed a series of experimetns under different conditions and calculated for each one the statistic ratio F_{exp}/F. During a particular experiment two parameters were kept as for standard conditions, i.e. $S_{\mathrm{Std}}=250\,\mu$mol, $V_{\mathrm{Std}}=50$ mL min^{-1}, and $C_{\mathrm{Std}}=10$ vol%, whereas the third was changed in the ranges: sample mass from 100 to 500 μmol, total gas flow rate 30–120 mL min^{-1}, and hydrogen concentration 3–25 vol%. In Fig. 8, the experimental data (reaction progress α vs. temperature) for one series of experiments are presented together with the curve α-T calculated using kinetic parameters fitting the experiment under standard conditions.

The results of the statistical calculations are presented in Table 3 and, using linear regression, in graphical form in Fig. 9.

On the basis of the results presented in Table 3 and in Fig. 9 we could determine the lower and upper confidence limits of the particular experimental variables (subscripts "l" and "u", respectively) and their confidence ranges Δ_{l} and Δ_{u}. Calculated values are listed in Table 4.

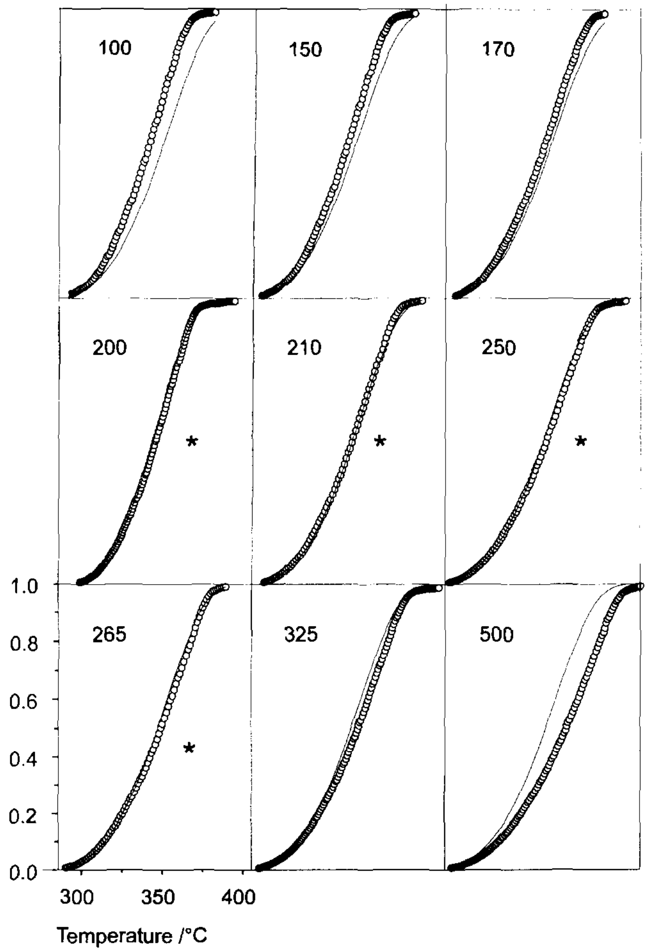

Fig. 8. Reaction progress α as a function of temperature for the reduction of NiO by hydrogen under the conditions: gas flow rate $V_{Std} = 50\,\mathrm{mL\,min^{-1}}$, hydrogen concentration $C_{Std} = 10\,\mathrm{vol\%}$, heating rate $\beta = 5.5\,\mathrm{K\,min^{-1}}$, sample mass S changed from 100–500 μmol (marked in each section). Experimental data are presented as empty circles, solid lines represent the relationship α–T calculated from the kinetic parameters obtained under standard conditions. For the plots marked by asterisks the criterion $F_{exp}/F < 1$ is fulfilled. The scale for all plots is the same as that shown in the lower left figure.

The confidence limits of the experimental variables listed in Table 4 indicate with the probability $P = 95\%$ the permitted changes of the particular experimental variables. For new S, V, or C the same set of kinetic parameters as for the "standard experiment" satisfactorily describes NiO reduction. Knowing the confidence limits for each variable we can construct the three-dimensional "isokinetic" space of the experimental conditions inside which the kinetic parameters can be accepted as constant. In order to construct this space we have to make the following assumptions:

(1) For each coordinate representing an experimental variable upper and lower confidence limits have to be given.

Table 3
Influence of the experimental conditions on the ratio F_{exp}/F; for values of the ratio > 1 the kinetic parameters obtained under "standard conditions" do not satisfactorily describe the reaction performed under new conditions

Sample mass S/μmol	F_{exp}/F	Gas flow rate V/(mL min^{-1})	F_{exp}/F	Hydrogen concentration C/vol%	F_{exp}/F
100	28.12	30	13.30	3	4.46
150	9.56	35	6.69	5	1.38
170	6.13	45	1.44	12	0.68
180	3.96	65	0.39	15	0.98
200	0.45	80	3.67	18	4.84
210	0.32	100	11.45	22	9.99
265	0.95	120	19.72	25	13.19
325	3.48				
400	13.91				
500	31.15				

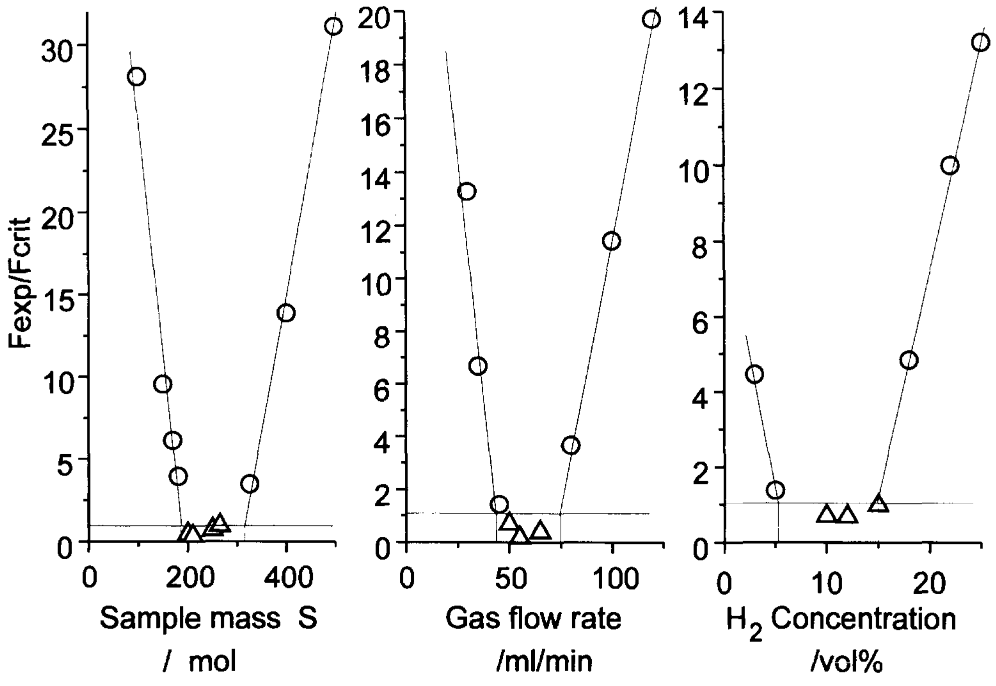

Fig. 9. Determination of parametric sensitivity of thermal analysis for the reduction of NiO by hydrogen applying the F-test with probability $P = 95\%$. Triangles indicate the conditions under which the kinetic parameters calculated for standard conditions properly describe the course of the reaction. Empty circles (criterion $F_{exp}/F > 1$) indicate that another set of the kinetic parameters should be applied.

Table 4
The lower and upper limits (confidence limits) for a change of particular experimental variables from their "standard values" $S_{\rm Std} = 250\,\mu$mol, $V_{\rm Std} = 50\,$mL min^{-1} and $C_{\rm Std} = 10$ vol% giving the same kinetic parameters as calculated for "standard conditions".

Experimental variables	Units	Lower limits	Upper limits	Lower difference	Upper difference
		$S_l \pm \Delta S_l$	$S_u \pm \Delta S_u$	$S_{\rm std} - S_l$	$S_u - S_{\rm std}$
S	μmol	200.1 ± 6.1	306.2 ± 7.5	49.9	56.2
		$V_l \pm \Delta V_l$	$V_u \pm \Delta V_u$	$V_{\rm std} - V_l$	$S_u - S_{\rm std}$
V	(cm^3 min^{-1})	45.9 ± 1.8	74.1 ± 2.3	4.1	24.1
		$C_l \pm \Delta C_l$	$C_u \pm \Delta C_u$	$C_{\rm std} - C_l$	$C_u - C_{\rm std}$
C	vol % H_2	5.3 ± 0.6	14.3 ± 0.8	4.7	4.3

(2) The confidence limits have to be determined taking into account the interdependence between the experimental variables (S, V and C have to be dependent).

(3) Using the parametric representation, the "isokinetic" space will be described by an ellipsoid (Fig. 10). We have three experimental parameters that can be increased or

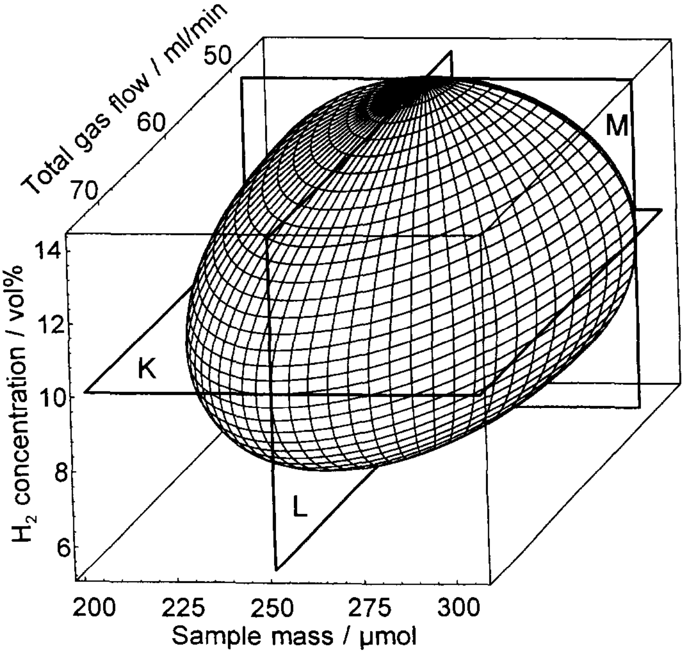

Fig. 10. "Isokinetic" space. The intersections of the frames K, L and M at the surfaces of the space characterize the lower and upper confidence limits for the respective experimental conditions. The intersection inside the confidence space represents the standard conditions. The course of the reduction performed under conditions lying outside this space cannot be properly described by the kinetic parameters calculated for the standard conditions.

reduced; consequently there are $2^3 = 8$ different possibilities of varying the experimental conditions.

In addition to the frames K, L and M parallel projection of the space can be effected in order to represent it by a two-dimensional illustration (Fig. 11).

4. Conclusion

The changing of experimental conditions such as sample mass, total gas flow or hydrogen concentration distinctly influences the course of the reduction of nickel oxide by hydrogen. Kinetic parameters of the reaction calculated from experiments performed with four heating rates under arbitrarily chosen standard conditions are differently dependent on the particular experimental variables. Using the statistical F-test, it is possible to present allowed changes of all three parameters (S, V and C) in three-dimensional space, i.e. to assign the "isokinetic" space in which, despite changes in the experimental conditions from their "standard" values, the kinetic parameters remain unchanged.

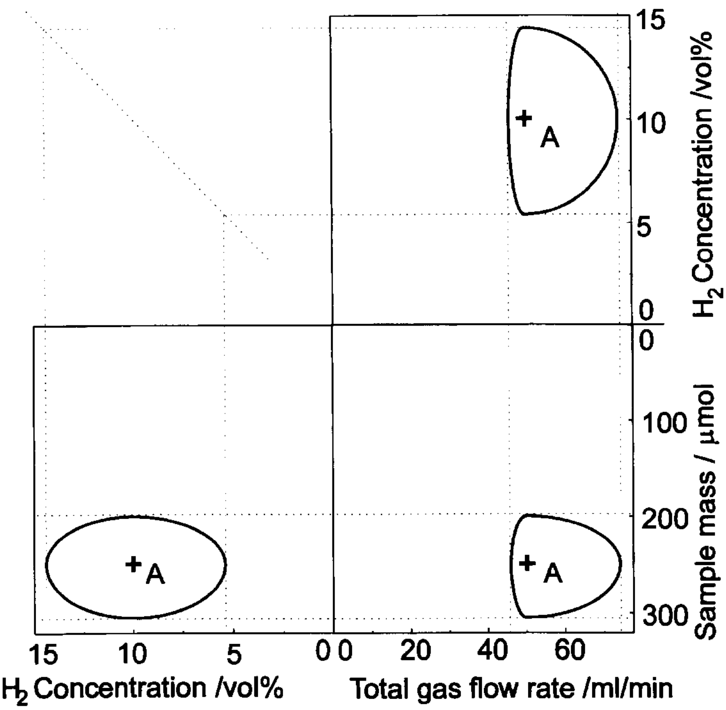

Fig. 11. "Isokinetic" space, 2-dimensional projection. The cross in each figure represents the standard conditions (point A, see also Fig. 1). It can be observed that the allowed increase or decrease of the sample mass or hydrogen concentration is quite symmetrical. Possible changes of the flow rate are not symmetrical.

The size of this ellipsoid-like domain is characteristic of the investigated reaction and for the set of the experimental conditions applied, i.e. it is not the same in different positions in *S–V–C* space. An increase in the size of the ellipsoid indicates lower parametric sensitivity of the reaction, i.e. its course depends less on changes in the experimental conditions. In commercial thermoanalysers and in common thermoanalytical practice experiments are performed under quite similar conditions (heating rate varies generally in the range 5–10 K min^{-1}, sample mass 20–50 mg, gas flow 30–50 mL min^{-1}) which can lead to their influence on the kinetics not being easily recognizable. The differences between experimental variables can be smaller than the size of the isokinetic ellipsoid — the same kinetic parameters will fit the experimental data well, and this leads to the conclusion that they can be regarded as the intrinsic properties of the investigated reaction.

The possible existence of this specific situation is a common source of incorrect interpretation of kinetic data of solid–gas reactions. They are not intrinsic for the investigated reaction, but for the whole system: i.e. the reaction and imposed experimental conditions. It is possible to minimize the influence of the last one by, e.g., performing the decomposition under vacuum or under a very well-defined pressure ramp (see Paulik [44], Ruoquerol [45,46]); that will somehow standardize the obtained data because of the possibility of performing the investigations in a well controlled atmosphere. But even in this case, despite much better reproducibility of the kinetic parameters, they can not be described as "true" generally valid constants, because they were calculated from data obtained under specific conditions and do not describe the course of differently performed experiments. One cannot describe the reduction of NiO under pure hydrogen and under an atmosphere containing 3 vol% H_2 by the same kinetic parameters.

Quantitative determination of the possible variation of all experimental conditions, in such a way that kinetic parameters remain unchanged, will be illustrated in a forthcoming paper [47].

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