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# Isothermal reduction kinetics of nickel oxide using hydrogen: Conventional and Weibull kinetic analysis

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## Abstract

The powder sample of nickel oxide was synthesized by sol-gel procedure. The isothermal reduction of nickel oxide using hydrogen was investigated by thermogravimetric analysis at five operating temperatures: 245, 255, 265, 275 and 300 °C. The kinetic triplet ( $E_a$ , A and  $f(\alpha)$ ) was determined using conventional and Weibull kinetic analysis. Both the kinetically procedures show that the reduction process considered can be explained with a two-step kinetic model. It is established that at lower temperatures (245 °C  $\leq T \leq 255$  °C), the reduction process considered is governed by two-parameter Šesták-Berggren autocatalytic model (first step) and at higher temperatures ( $T \geq 265$  °C), the reduction process is governed by Fn reaction model with different values of parameter n (second step). In this paper, the complex manner of dependence of the Weibull shape parameter ( $\beta$ ) on temperature is established. With alterations of Weibull shape parameter from lower temperatures ( $\beta > 1$ ) to higher temperatures ( $\beta < 1$ ), it was concluded that isothermal reduction process of NiO using hydrogen can be described by a multistep reaction mechanism. These results are confirmed by the evaluated density distribution functions (ddf) of apparent activation energies ( $E_a$ ), which show variations in basic characteristics at lower and higher operating temperature regions. Also, in this paper, it was shown that the shape parameter ( $\beta$ ) of Weibull distribution function can represent the behaviour index, which indicates the kinetic pattern of the mechanism controlling the process studied.  $\mathbb{C}$  2007 Elsevier Ltd. All rights reserved.

Keywords: Oxides; Thermogravimetric analysis (TGA); Surface properties

## 1. Introduction

Metal oxides are used as catalysts in a large variety of commercial processes for the conversion of hydrocarbons [1,2]. Selective oxidation, ammoxidation and selective dehydrogenation probably constitute the most important catalytic applications of metal oxides [2]. In addition, due to their low cost, metal oxides are also used as supports of many other catalytic materials (metals, sulfides, carbides, nitrides, etc.) [1,2]. In most cases, pure stoichiometric oxides do not exhibit high catalytic activity [2]. For the preparation of active oxide catalysts, the partial reduction of nickel oxide under hydrogen at elevated temperatures is the effective method for this preparation [3–5]. In general

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terms, two different kinetic models have been proposed for the reduction of oxides: the "nucleation model" [4,6] and the "interface-controlled model" [7]. The first reported systematic measurements of bulk NiO reduction was by Benton and Emmett [8]. These authors are measured water formation as an indication of the extent of reaction for a sample of NiO made by heating nickel nitrate at 400 °C. They derived very important conclusions: (a) reduction occurs at the interface between NiO and previously reduced Ni; (b) there is an "autocatalytic" effect; (c) there is an induction (i.e. nucleation) period that depends on the nature of the sample and temperature and (d) added water reduces the reduction rate and increases the induction period. Koga and Harrison reviewed general reactions between solids and hydrogen and represented the induction process as generation of nickel atoms on the outer surface of NiO grains [9]. Following nucleation, Ni clusters grow two dimensionally across the surface until they overlap, at

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which point, hydrogen rapidly dissociates on Ni and the interface proceeds quickly into the grain [9]. Bandrowski et al. [10] measured water produced during the reduction to generate sigmoidal conversion curves they explained with a two-step kinetic model. The first step, reaction between NiO and hydrogen atoms adsorbed on NiO, predominates in the early part of the reduction and is proportional to the square root of the hydrogen pressure. The second step is a reaction at the metal-oxide interface between NiO and hydrogen atoms adsorbed on the previously reduced NiO. The above models emphasized the chemical mechanism and kinetics of the reduction process, but there is a little uniformity in the physical properties of NiO grains and pellets used. Nevertheless, it was suspected that morphological factors were just as important as topological properties in the determining the course of reduction. These factors were demonstrated by Moriyama and Yamaguchi [11], who found that reduction rate constants are inversely proportional to grain diameter above about 10 µm. Such dependence is predicted by the shrinking-core model [12]. Villarrubia and Ho [13] have evidenced the half-order dependence of the reduction rate on hydrogen pressure, and then they revealed the dissociative adsorption of hydrogen followed with water formation. For low oxygen coverage these authors have demonstrated the existence of two periods: an induction period corresponding to a negligible reduction, and a reactive period. This experimental result was well fitted by Monte Carlo simulations. Vreeburg et al. [14] showed that, at high temperature (above 600 K), dissolution of oxygen in the nickel crystal has a key role and that reaction kinetics of the oxidized Ni (111) and Ni (100) are alike. Richardson et al. [15] conducted a series of experiments using isothermal H<sub>2</sub> consumption and magnetization measurements to determine, respectively Ni-O bond rupture (NiO conversion) and the growth of nucleated Ni atoms. They found the growth process lagged NiO conversion by a time interval that increased with decreasing temperature, lower gas flow rates and the presence of H<sub>2</sub>O added to the reducing gas. Rodriguez et al. [16] showed that in experiments with NiO (100) crystal and NiO powders, oxide reduction is observed at atmospheric pressures and elevated temperatures (250-350 °C), but only after an induction period. These authors showed that the presence of O vacancies leads to an increase in the adsorption energy of H<sub>2</sub> and substantially lowers the energy barrier associated with the cleavage of the H–H bond. Richardson et al. [17] studied the hydrogen reduction of porous bulk NiO particles with in situ hot-stage X-ray diffraction (XRD) in the temperature range 175-300 °C. The results obtained by these authors indicated that reduction in the absence of water added to the reducing gas followed several steps: (1) an induction period associated with the initial reduction of NiO and the appearance of Ni metal clusters; (2) acceleration of the reduction rate as the size of the clusters increases, and (3) a pseudo-first-order process in which NiO disappeared and Ni appeared in concert until

reduction slowed at a fractional conversion of about 0.8. When  $2.2 \times 10^{-2}$  atm of H<sub>2</sub>O was added to the reducing gas, induction times increased by approximately a factor of two and reduction rates decreased, with an apparent activation energy of  $126 \pm 27 \text{ kJ mol}^{-1}$  compared to 85+6 kJ mol<sup>-1</sup> without added water [17]. Utigard et al. [18] investigated the reduction kinetics of NiO granules formed by vapour deposition from a chloride solution, using thermal gravimetry. They reported that in the temperature range 400–600 °C, the rate of reduction increased with increasing temperature and increasing hydrogen pressure. Microscopic analysis showed that in this temperature range the reaction followed the shrinkingcore model [18]. The same authors found that the activation energy for the reduction process has a value of  $90 \text{ kJ mol}^{-1}$ , in the above temperature range.

Based on the facts given above, in this paper, the kinetics and mechanism of powder nickel oxide reduction, which was obtained by gel-combustion procedure with hydrogen at the atmospheric pressure, were investigated by isothermal thermogravimetric analysis. The objective of this investigation was to determine the kinetic triplet (Arrhenius parameters A and  $E_a$ , and the reaction model,  $f(\alpha)$ ) by the conventional kinetic analysis associated with Weibull kinetic analysis, and the density distribution function (ddf) of apparent activation energies at different experimental temperatures, based on the known Weibull distribution of one variable (the reaction time—t), for the reduction process of powder NiO in hydrogen atmosphere.

# 2. Experimental

#### 2.1. Materials and methods

The NiO samples were obtained by gel-combustion method described elsewhere [19]. A green-coloured transparent gel was obtained by drying an aqueous solution of nickel nitrate hexahydrate (Fluka, 99.5%) and citric acid (Fluka, 99.5%), dissolved in a mole ratio 1.8:1. This gel further underwent to a self-ignition by heating in air up to  $300 \,^{\circ}$ C, and by an additional heating up to  $500 \,^{\circ}$ C, produces a very fine nickel oxide powders. The particle size of the obtained nickel oxide powder samples was  $20 \,\mu$ m.

#### 2.2. Thermogravimetric measurements

The reduction experiments were carried out in a TA SDT 2960 device, capable of simultaneous TGA-DTA analysis in the temperature range 25–1500 °C. The nickel oxide samples were reduced directly within the thermobalance, in korund pans, under (99.9995 vol%) flow rate of hydrogen of 100 mL min<sup>-1</sup>. The mass loss experiments were carried out at five different temperatures: T = 245, 255, 265, 275 and 300 °C. The sample mass used for thermogravimetric investigations was about  $25\pm0.5$  mg.

## 3. Theory

## 3.1. Rate laws and conventional kinetic analysis

In isothermal thermogravimetric (TG) experiments the change of the sample mass is registered as a function of time (t). The fractional extent of reaction (conversion) is expressed as

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty},\tag{1}$$

where *m* is an actual mass at time *t*,  $m_0$  the initial sample mass and  $m_{\infty}$  the mass at the end of isothermal experiments.

The differential kinetic equation can be expressed as [20,21]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha),\tag{2}$$

where *t* is the time, *T* the temperature, and  $f(\alpha)$  the reaction model. The explicit temperature dependence of the rate constant is introduced by replacing k(T) with the Arrhenius equation, which gives

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A \, \exp\!\left(\frac{E_a}{RT}\right) f(\alpha),\tag{3}$$

where A (the pre-exponential factor) and  $E_a$  (the apparent activation energy) are the Arrhenius parameters and R is the gas constant. The main implication of Eq. (3) is that the reaction rate at a constant conversion degree is only a function of the temperature, and this is the basic assumption of the so-called isoconversional methods. This assumption holds only for a single-step reaction. For multistep kinetics the dependence of the apparent activation energy ( $E_a$ ) on conversion ( $\alpha$ ) reflects the variation in relative contribution of single steps to the overall reaction rate. The function  $f(\alpha)$  in Eq. (3) is an analytical expression describing the kinetic model of the studied reduction process (Table 1). The mutual correlation of Arrhenius kinetic parameters (apparent activation energy and preexponential factor) and kinetic model does not allow an accurate kinetic analysis to be performed by using only one experimental TG [20]. This problem can be solved by calculating the apparent activation energy from several isothermal experiments and by determining the most probable kinetic model.

By integrating Eq. (3) in isothermal conditions, the following equation is obtained:

$$g(\alpha) = \int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = A \, \exp\left(-\frac{E_a}{RT}\right) t,\tag{4}$$

where  $g(\alpha)$  is the integrated form of the reaction model (Table 1). The apparent activation energy of the reduction process in isothermal conditions can be calculated by isoconversional (the model-free) method which follows from logarithmic form of Eq. (4):

$$-\ln t = \ln \left[\frac{A}{g(\alpha)}\right] - \frac{E_a}{RT}.$$
(5)

The slope of  $-\ln t$  vs. 1/T for the same value of  $\alpha$  gives the value of apparent activation energy. This procedure can be repeated for various values of  $\alpha$ . Therefore, the method provides a check of invariance of  $E_a$  with respect to  $\alpha$  in the  $0.30 < \alpha < 0.70$  range, which is one of the basic assumptions in kinetic analysis of thermogravimetric data.

To choose an appropriate reaction model, one can plot  $\alpha$  as a function of a reduced time variable  $t/t_{\alpha}$ , where  $t_{\alpha}$  is the time required to reach a specified conversion (e.g.,  $\alpha = 0.9$ ). The method of isothermal reduced-time plots (RTPs) is broadly used in solid state kinetics [21–24].

Combining Eqs. (3) and (4) a new function  $Z(\alpha)$  can be defined as

$$Z(\alpha) = \left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)t = f(\alpha)g(\alpha). \tag{6}$$

For practical reasons this function is normalized within the (0,1) interval. It was shown by Málek [25] that the maximum

Table 1

Expressions for  $f(\alpha)$  and  $g(\alpha)$  functions for some of the common mechanisms operating in the solid state reactions

No.	Symbol	Reaction model	$f(\alpha)$	$g(\alpha)$
1	P1	Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
2	P2	Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
3	P3	Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
4	P4	Power law	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
5	R1	Zero order (Polany–Winger equation)	1	α
6	R2	Phase-boundary controlled reaction (contracting area, i.e. bi-dimensional shape)	$2(1-\alpha)^{1/2}$	$[1-(1-\alpha)^{1/2}]$
7	R3	Phase-boundary controlled reaction (contracting volume, i.e. tri-dimensional shape)	$3(1-\alpha)^{2/3}$	$[1-(1-\alpha)^{1/3}]$
8	F1	First order (Mampel)	$(1-\alpha)$	$-\ln(1-\alpha)$
9	A2	Johnson–Mehl–Avrami (JMA) ( $m = 2$ )	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln (1-\alpha)]^{1/2}$
10	A3	Johnson–Mehl–Avrami (JMA) ( $m = 3$ )	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln (1-\alpha)]^{1/3}$
11	A4	Johnson–Mehl–Avrami (JMA) ( $m = 4$ )	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln (1-\alpha)]^{1/4}$
12	D1	One-dimensional diffusion	1/2α	$\alpha^2$
13	D2	Two-dimensional diffusion (bi-dimensional particle shape) Valensi equation	$1/[-\ln (1-\alpha)]$	$(1-\alpha) \ln (1-\alpha) + \alpha$
14	D3	Three-dimensional diffusion (tri-dimensional particle shape) Jander equation	$3(1-\alpha)^{1/3}/2[(1-\alpha)^{-1/3}-1]$	$[1-(1-\alpha)^{1/3}]^2$
15	D4	Three-dimensional diffusion (tri-dimensional particle shape) Ginstling-Brounshtein	$3/2[(1-\alpha)^{-1/3}-1]$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$

Table 2

Model	Symbol	$f(\alpha)$	$\alpha_p^{\infty}$	$\alpha_M$
Reaction order	Fn	$(1-\alpha)^n$	$1 - n^{1/(1-n)}$	0
Johnson–Mehl–Avrami	JMA $(m > 1)$	$m(1-\alpha)[-\ln (1-\alpha)]^{1-1/m}$	0.633	$1 - \exp(1/m - 1)$
Šesták–Berggren	SB $(M, N)^{a}$	$\alpha^{M}(1-\alpha)^{N}$	$(0,\alpha_n)$	M/(M+N)
Two-dimensional diffusion	D2	$1/[-\ln(1-\alpha)]$	0.834	0
Jander eqn.	D3	$3(1-\alpha)^{1/3}/2[(1-\alpha)^{-1/3}-1]$	0.704	0
Ginstling-Brounshtein	D4	$3/2[(1-\alpha)^{-1/3}-1]$	0.776	0

The kinetic models and maxima of  $Z(\alpha)$  function  $(\alpha p \infty)$  and  $Y(\alpha)$  function  $(\alpha M)$ 

<sup>a</sup>The SB model is valid for 0 < M < 1.

of this function (usually labeled  $\alpha_p^{\infty}$ ) has characteristic values for basic kinetic models shown in Table 2.

It is seen that the  $\alpha_p^{\infty}$  is constant for D2, D3, D4 and JMA(*m*) model. On the other hand, it depends on particular value of kinetic exponent for the Fn or SB (*M*, *N*) model. Therefore, the function  $Z(\alpha)$  is useful for classification of possible kinetic model of the investigated process. In isothermal conditions, however, the term  $A \exp(-E_a/RT)$  in Eq. (3) is constant and the reaction rate  $(d\alpha/dt)$  is proportional to the  $f(\alpha)$  function:

$$Y(\alpha) = \left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) \approx f(\alpha). \tag{7}$$

Therefore, if the reaction rate is plotted as a function of  $\alpha$  its shape corresponds to the  $f(\alpha)$  function. It is convenient to normalize the  $Y(\alpha)$  plot within the (0,1) interval. The shape of this plot is characteristic for each kinetic model and it can be used as a diagnostic tool for the kinetic model determination. The following rules can be formulated [25–27] in this respect:

- (A) If the  $Y(\alpha)$  function has a maximum at  $\alpha_M = 0$  then it can be convex, linear or concave. Convex dependence corresponds to  $Fn \ (n < 1)$  model, linear dependence to the JMA (m = 1) or  $Fn \ (n = 1)$  model (formally identical models) and concave dependence to the JMA (m < 1), D2, D3, D4 and  $Fn \ (n > 1)$  models.
- (B) If the  $Y(\alpha)$  function exhibit a maximum in interval  $\alpha_M \in (0, \alpha_p)$  (where  $\alpha_p$  is the conversion of reaction at the maximum  $d\alpha/dt$ ) then it corresponds to the SB (M, N) or JMA (m>1) model. The mathematical conditions for these maxima are shown in Table 2.

Thus, the shape of both  $Y(\alpha)$  and  $Z(\alpha)$  functions can be used conveniently for the determination of the most probable kinetic model [25]. The kinetic exponent for the Fn model can be obtained from the maximum,  $\alpha_p^{\infty}$ , of the  $Z(\alpha)$  function and the kinetic exponents of JMA (m > 1) and SB (M, N) are obtained from maximum,  $\alpha_M$ , of the  $Y(\alpha)$  function (see Table 2).

### 3.2. Weibull kinetic analysis

Assuming that the reaction times of investigated reduction process are randomly distributed by the laws of Weibull distribution function [28], and assuming that the value of Weibull distribution function of reaction times (*t*) (random variable) is proportional to the fractional extent of reaction ( $\alpha$ ), it can be written as

$$\alpha(t) = F(t) = 1 - \exp\left[-\left(\frac{t-\gamma}{\eta}\right)^{\beta}\right],\tag{8}$$

where F(t) is the cumulative Weibull distribution function, t the time,  $\beta$  the shape parameter (because it determines the shape of the distribution),  $\eta$  the scale parameter (because it scales the t variable) and  $\gamma$  is a third parameter, used to define a suitable zero point. The constant  $\gamma$  is called the location parameter. The location parameter  $\gamma$  is often equal to zero. The Weibull distribution is exponential in shape for small  $\beta$  and becomes more Gaussian as  $\beta$  increases. Techniques to determine the desired Weibull parameters include the Weibull plot, maximum likelihood estimation (MLE), linear estimator, method of moments (MOM) and direct non-linear curve fitting. The Weibull plot method [29], direct non-linear curve-fitting method [30,31] and maximum likelihood (ML) method [32] are used in this study for estimating the Weibull distribution parameters. The Weibull plot method is the most common and easiest way to obtain the Weibull parameters ( $\beta$  and  $\eta$ , for  $\gamma = 0$ ). A Weibull plot can be drawn by rearranging Eq. (8) and taking natural logarithms twice. Thus,  $\beta$  and  $\eta$  can be determined by fitting the following equation:

$$\ln[-\ln(1 - F(t))] = \beta \ln\left(\frac{1}{\eta}\right) + \beta \ln(t).$$
(9)

The non-linear curve-fitting method was based on the direct numerical fitting of the experimental isothermal conversion  $(\alpha - t)$  curves at different temperatures to the expression of cumulative Weibull distribution function. The Microcal Origin Program 7.0 was used in this paper for non-linear curve-fitting analysis.

The method of ML [32] is a commonly used procedure because it has very desirable properties. The likelihood function is the mathematical expression of the probability of obtaining the observed data. From this method, the shape parameter ( $\beta$ ) of Weibull distribution can be obtained by the expression [32]:

$$\frac{\sum_{i=1}^{n} t_{i}^{\beta} \ln t_{i}}{\sum_{i=1}^{n} t_{i}^{\beta}} - \frac{1}{\beta} - \frac{1}{n} \sum_{i=1}^{n} \ln t_{i} = 0,$$
(10)

where  $t_i$  is the random variable (in our case this is the time), and *n* is the number of experimental data points. Eq. (10) may be solved to get the estimate of  $\hat{\mu}_k = \beta$  ( $\hat{\mu}_k$  is the first moment). This can be accomplished by the use of standard iterative procedures (i.e. Newton–Raphson method). Once  $\beta$  is determined,  $\eta$  can be estimated using the equation given below [32]:

$$\eta = \frac{\sum_{i=1}^{n} t_i^{\beta}}{n}.$$
(11)

If the time dependence of the fractional extent of reaction is well described by Eq. (8) with  $\gamma = 0$ , then corresponding rate of process can be given by the first derivative of this function with respect to the time variable. Thus, we can write

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{1}{\eta} \beta \left(\frac{1}{\eta}t\right)^{\beta-1} \exp\left[-\left(\frac{1}{n}t\right)^{\beta}\right].$$
(12)

Eq. (12) also represents the two-parameter Weibull probability density function (pdf). The Arrhenius–Weibull differential rate equation or the Arrhenius–Weibull probability density function can be obtained by setting  $1/\eta = A \exp(-E_a/RT)$  in Eq. (12):

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{T} \equiv f(t, T = \mathrm{const}) = A \exp\left(-\frac{E_{a}}{RT}\right)$$
$$\times \beta \left[A \exp\left(-\frac{E_{a}}{RT}\right)t\right]^{\beta-1}$$
$$\times \exp\left\{-\left[A \exp\left(-\frac{E_{a}}{RT}\right)t\right]^{\beta}\right\},\tag{13}$$

where  $1/\eta$  is the rate constant  $(1/\eta \sim k)$ . For calculating the Arrhenius–Weibull differential rate equation, the preexponential factor (A) and the apparent activation energy  $(E_a)$  must be known a priori.

#### 4. Results and discussion

The experimentally obtained isothermal conversion  $(\alpha - t)$  curves for temperatures between 245 and 300 °C when using 99.99% H<sub>2</sub> gas are presented in Fig. 1.

It is seen that the rate of conversion increases with increasing temperature and between 265 and 300 °C, approximately 100% conversion is achieved in less than 1 h. The experimental rate-time  $(d\alpha/dt-t)$  curves obtained at different temperatures (in the range 245–300 °C) for the reduction process of NiO using hydrogen are shown in Fig. 2.

The rate-time curves at lower temperatures (245 and 255 °C) (Fig. 2) clearly show that the maximum rate of process  $(v_{max})$  existed for  $t_{max} > 0$ , while the curves at higher temperatures (265, 275 and 300 °C) have  $v = v_{max}$  at t = 0. The values of  $v_{max}$ ,  $t_{max}$ ,  $t_{m/2}$  ( $t_{m/2}$  is the time taken for the rate to drop to half its maximum value (i.e.  $v_{max}/2$ )—characteristic time value for  $d\alpha/dt-t$  curves at 265, 275 and 300 °C) and  $t'_{m/2}$  ( $t'_{m/2}$  is the time on the



Fig. 1. The isothermal conversion  $(\alpha - t)$  curves for reduction of nickel oxide in hydrogen atmosphere, at operating temperatures 245, 255, 265, 275 and 300 °C.



Fig. 2. The experimental rate-time  $(d\alpha/dt \text{ vs. } t)$  curves for reduction of nickel oxide in hydrogen atmosphere obtained at different operating temperatures (T = 245, 255, 265, 275 and 300 °C).

descent for  $d\alpha/dt-t$  curves at 245 and 255 °C) for the rate-time curves of reduction process of NiO in hydrogen atmosphere at five different temperatures are presented in Table 3.

Table 3 The values of  $v_{max}$ ,  $t_{max}$ ,  $t_{m/2}$  and  $t'_{m/2}$  for experimental rate-time (d $\alpha$ /dt vs. t) curves at different operating temperatures 245, 255, 265, 275 and 300 °C

Temperature (°C)	$v_{max}$ (min <sup>-1</sup> )	$t_{max}$ (min)	$t_{m/2}$ (min)	$t'_{m/2}$ (min)
245 <sup>a</sup>	0.0220	12.00	7.49	42.40
255 <sup>a</sup>	0.0440	5.00	1.25	21.82
265 <sup>b</sup>	0.0763	0	6.09	_
275 <sup>b</sup>	0.1382	0	4.23	_
300 <sup>b</sup>	0.1744	0	3.90	-

 ${}^{a}t_{m/2}$  on the ascent and  $t'_{m/2}$  on the descent of rate-time curves.

 ${}^{\rm b}t_{m/2}$  valid only for rate-time curves at 265, 275 and 300 °C.

From Table 3, it can be seen that the values of  $t_{m/2}$  and  $t'_{m/2}$  decreased from 245 to 255 °C. Also, the values of  $t_{m/2}$ decreased with increasing temperatures from 265 to  $300 \,^{\circ}$ C. On the other hand, the values of  $v_{max}$  increases with increasing temperatures. The results presented in Table 3 are useful for basic classification of kinetic models. Thus, the results from Table 3, at 245 and 255 °C, designated the sigmoid group of kinetic models (this group have  $v = v_{max}$ at  $t = t_{max} > 0$ ). On the other hand, the results at 265, 275 and 300 °C (Table 3) designated on the deceleratory group of kinetic models [33]. Furthermore, the velocity of water removal from the reaction surface increases with increase in operating temperature. Particularly, at lower operating temperatures (at 245 and 255 °C), the adsorbed  $H_2O$ molecules produced by the reaction retard the growth process, slowed the reduction rate (Fig. 2) and exhibited the beginning of an induction period (Fig. 1). This induction period is longer at lowest temperature (245 °C) and in the presence of greater amount of water originating from the reaction. Clearly, water molecules on the surface increase the induction period and decrease the reduction rate, and the effects are less significant at higher operating temperatures. Precisely, higher temperatures favour rapid water removal and it can be seen that at temperatures  $T \ge 265 \,^{\circ}\text{C}$ . The induction period disappeared when the reduction rate increases (Fig. 2). Fig. 3 shows the experimental RTPs obtained at the isothermal operating temperatures 245, 255, 265, 275 and 300 °C, and they are compared with theoretical RTPs in Table 1.

The experimental RTPs obtained at various operating temperatures should be identical provided the kinetic triplet does not vary with temperature [23]. However, in our case, we can observe the great disparity among the experimental RTPs (Fig. 3). From Fig. 3, it can be seen that no experimental RTP corresponds to the reaction models in Table 1. Also, the presented experimental RTPs vary with temperature. These changes can be a consequence of variation with temperature of at least one component in kinetic triplet.

Fig. 4(a and b) shows the apparent activation energy  $E_a$  and  $\ln[A/g(\alpha)]$  as functions of the fractional extent of reaction ( $\alpha$ ) calculated by isoconversional method from the slope and intercept of the  $-\ln t$  vs. 1/T plots.



Fig. 3. Comparison of theoretical reduced-time plots (RTPs) for reaction models described in Table 1 with RTPs experimentally determined at five isothermal operating temperatures 245, 255, 265, 275 and 300 °C.

Any point in this figure is obtained from the above relationship within the certain error limits (specified by bars). As mentioned in Section 3.1, the apparent activation energy should be invariant with respect to  $\alpha$  in the  $0.30 < \alpha < 0.70$  range. In fact the value of  $E_a$  decreases with fractional conversion, but in the above-restricted interval the apparent activation energy is less  $\alpha$  dependent (Fig. 4a). The average value of the apparent activation energy  $(E_a)$  in the  $0.30 < \alpha < 0.70$  range is found to be  $E_a = 100.7$  kJ mol<sup>-1</sup>. Alternatively,  $\ln[A/g(\alpha)] - \alpha$  plot demonstrates identical characteristics (Fig. 4b), and this suggests that the apparent activation energy  $(E_a)$  and the pre-exponential factor (A) both depend in the same way on the fractional extent of reaction  $(\alpha)$ .

Figs. 5 and 6 present  $Y(\alpha)$  and  $Z(\alpha)$  functions normalized within the (0,1) interval, for the reduction process of NiO using hydrogen at the isothermal operating temperatures 245, 255, 265, 275 and 300 °C.

The  $Y(\alpha)$  function presented its maximum,  $\alpha_M$ , located at 0.10 and 0.12 for T = 245 and 255 °C, respectively (Fig. 5). The  $Z(\alpha)$  function presented its maximum,  $\alpha_p^{\infty}$ , located at 0.46 and 0.54 for T = 245 and 255 °C, respectively (Fig. 6). If  $Y(\alpha)$  function exhibits its maximum in  $0 < \alpha_M < \alpha_p$  interval, the Šesták-Berggren (SB) or Johnson–Mehl– Avrami (JMA) are the most probable kinetic models [25,34,35]. The validity of the JMA kinetic model can easily be verified by checking the maximum  $\alpha_p^{\infty}$  that falls in the 0.61 $\leq \alpha_p^{\infty} \leq 0.65$  interval [36]. For reduction process of NiO, at T = 245 and 255 °C,  $\alpha_p^{\infty}$  is shifted to lower values,



Fig. 4. (a) Apparent activation energy calculated from isothermal thermogravimetric data plotted as a function of fractional conversion for reduction process of NiO samples using hydrogen and (b) the isoconversional intercepts plotted as a function of fractional conversion for reduction process of NiO samples using hydrogen. The points were calculated by the isoconversional method using Eq. (5) and the lines are drawn as guides for the eye. The dot line shows the average  $E_a$  value in the restricted interval  $0.30 < \alpha < 0.70$ , used for kinetic calculations.

and this does not correspond to the JMA kinetic model. Therefore, the  $Y(\alpha)$  and  $Z(\alpha)$  functions, at T = 245 and 255 °C, satisfy the condition for two-parameter autocatalytic model (Sesták-Berggren (SB) equation), which for a reaction with zero initial rate [20,37,38],

$$f(\alpha) = \alpha^M (1 - \alpha)^N, \tag{14}$$

where M and N represent the so-called reaction orders by similarity with the *n*th order model [39]. *M* is the reaction order for the induction period and N is the reaction order for the crystallization reaction. Eq. (14) was derived on the basis that the most common heterogeneous reactions take place in three stages: An induction or nucleation period (during which reaction centres form within the solid), the interfacial reaction (where these centres expand so that the interfaces between product and reactant increase) and finally decay (when the centres overlap and the interfaces between product and reactant begin to decrease).

The kinetic parameters N and  $\ln A$  can be calculated from the logarithmic form of Eq. (3) considering  $f(\alpha) = \alpha^{M} (1-\alpha)^{N}$  after rearrangement yields [25]:

$$\ln\left[\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)\exp\left(\frac{E_a}{RT}\right)\right] = \ln A + N \ln[\alpha^p(1-\alpha)],\tag{15}$$



Fig. 5. Normalized  $Y(\alpha)$  functions obtained by transformation of isothermal TG data for reduction process of NiO in hydrogen atmosphere at different operating temperatures.



Fig. 6. Normalized  $Z(\alpha)$  functions obtained by transformation of isothermal TG data for reduction process of NiO in hydrogen atmosphere at different operating temperatures.

where  $p = \alpha_M / (1 - \alpha_M)$ . From the slope and intercept of the linear dependence  $\ln[(d\alpha/dt) \exp (E_a/RT)]$  vs.  $\ln[\alpha^p(1-\alpha)]$ we can obtain the kinetic parameters N and  $\ln A$ . The value of parameter M can be obtained from relation M = pN.

The values of N and  $\ln A$  were determined using the average value of the apparent activation energy  $(E_a)$ from the isoconversional method, in the  $0.30 < \alpha < 0.70$ range.

Table 4 lists the kinetic parameters (*M*, *N* and  $\ln A$ ) evaluated from Eq. (15) for reduction process of powder NiO in hydrogen atmosphere, at T = 245 and  $255 \,^{\circ}\text{C}$ .

Mathematically, the autocatalytic behaviour is much more complex, and because of this complexity, in the autocatalytic adjustment a single activation energy was assumed for the whole process in the considered temperature range [39]. The increase in the value of the kinetic parameter M (Table 4) indicates a more important role of the product on the overall kinetics with an autocatalytic behaviour. It seems that a higher value of the kinetic parameter N > 1 means increasing complexity of the reduction process and this can be caused, for example, by the influence of surface nucleation. In fact, the twoparameter autocatalytic SB model includes the JMA as a special case whose applicability involves a narrowest limit for  $\alpha_M$  and  $\alpha_p^{\infty}$  values in relation to the SB [34]. However, the physical meaning attributed for M and N should not go beyond those described above, unless more detailed conclusions concerning the reduction mechanism are based on other types of complementary evidence, including microscopic observations and all other relevant information.

The  $Y(\alpha)$  functions shows the concave behavior and exhibits a maximums at  $\alpha_M = 0$  for operating temperatures of 265, 275 and 300 °C (Fig. 5). On the other hand, maxima of  $Z(\alpha)$  is  $\alpha_p^{\infty} < 0.61$  for T = 265, 275 and 300 °C ( $\alpha_p^{\infty} = 0.57, 0.49$  and 0.60, respectively) (Fig. 6). The most probable kinetic model is, therefore, Fn (n>1) model. Knowing the kinetic model, the equation for isothermal  $\alpha(t)$  curve is obtained from Eq. (4). For the Fn model it can be written in the following form:

$$\alpha(t) = 1 - [1 - t(1 - n)A \exp(-x)]^{1/(1-n)}.$$
(16)

The value of reduced activation energy is constant in isothermal conditions ( $x = E_a/RT$ ) and it can easily be calculated for the average value of apparent activation energy obtained by isoconversional method (see above). The values of parameters *n* and *A* can then be obtained by non-linear regression of experimental data. For non-linear regression of experimental data, the Levenberg–Marquardt (LM) algorithm was used.

Table 4

The parameters of the reaction model  $f(\alpha) = \alpha^M (1-\alpha)^N$  (Eq. (14)) as well as the ln *A* value resulting from Eq. (15) for reduction of nickel oxide samples in hydrogen atmosphere at 245 and 255 °C

Temperature (°C)	М	Ν	$\ln A \; (\mathrm{A}  \mathrm{min}^{-1})$
245	$0.12 \pm 0.01$	$1.10 \pm 0.03$	$20.73 \pm 0.02$
255	$0.18 \pm 0.02$	$1.26 \pm 0.01$	$20.91 \pm 0.01$

The values of kinetic parameters obtained by non-linear regression of isothermal reduction data, in temperature range of 265 °C  $\leq T \leq 300$  °C using Eq. (16), for constant value of apparent activation energy ( $E_a = 100.7 \text{ kJ mol}^{-1}$ ) are shown in Table 5.

For the *n*th order kinetics of chemical reaction,  $f(\alpha)$  is given by the expression

$$f(\alpha) = (1 - \alpha)^n. \tag{17}$$

The choice of the model depends on the type of chemical reaction. In the *n*th order reaction, all the reacting species are converted at the beginning of the reaction and the reaction rate will be maximum at the initial stage, i.e. for an isothermal test, Eq. (17) predicts a maximum of the reaction rate at time equal to zero. Then, if an isothermal rate–time curve shows a maximum of the reaction rate at some point other than the initial one, the kinetic model given by Eq. (17) cannot be applied. On the other hand, in the autocatalytic reaction, the maximum rate of conversion will be other than zero due the involvement of product of reaction in the ongoing reaction. The results of our isothermal rate–time ( $d\alpha/dt-t$ ) curves (Fig. 2) confirms the above statements.

Fig. 7 shows the comparison of experimental data (symbols) and calculated (lines)  $\alpha(t)$  plots for reduction process of NiO samples at T = 265, 275 and 300 °C. The  $\alpha(t)$  curves were calculated using Eq. (16) for the kinetic parameters shown in Table 5.

There is quite good agreement between experimental data and the prediction of the Fn model. Some discrepancies are observed only for NiO sample at  $T = 275 \,^{\circ}$ C, for higher values of  $\alpha$ .

Fig. 8 shows the experimental RTPs at the isothermal operating temperatures of 265, 275 and 300 °C, which were compared with theoretical RTPs for Fn group of reaction models with n = 1.17, 1.36 and 1.94.

Excellent agreement exists between experimental and theoretical RTPs for F1.17, F1.36 and F1.94 models at considered temperatures.

It should be emphasized that the variations in the actual amount of product with operating temperatures can affect the reduction mechanism and change the kinetic parameters obtained. From the results given in Tables 4 and 5, we can observe that the reaction orders M and N (and reaction order n for temperatures above 265 °C) are functions of the operating temperature. The reaction order

Table 5

The kinetic parameters obtained by non-linear regression of isothermal data using Eq. (16) and constant value of apparent activation energy (100.7 kJ mol<sup>-1</sup>) for reduction process of NiO using hydrogen, at T = 265, 275 and 300 °C

Temperature/°C	п	$\ln A \ (\mathrm{A} \min^{-1})$
265	$1.36 \pm 0.01$	$20.56 \pm 0.02$
275	$1.94 \pm 0.02$	$20.93 \pm 0.01$
300	$1.17 \pm 0.01$	$20.46 \pm 0.03$



Fig. 7. Isothermal conversion curves for reduction process of NiO using hydrogen at  $(\Box)$  265 °C;  $(\odot)$  275 °C and  $(\triangle)$  300 °C. Full lines were calculated using Eq. (16) for the kinetic parameters shown in Table 5.



Fig. 8. Comparison of theoretical reduced-time plots (RTPs) for Fn group of reaction models with n = 1.17, 1.36 and 1.94, with RTPs experimentally determined at isothermal operating temperatures 265, 275 and 300 °C.

M can represent the catalytic effect of the reduced material and N (and n for higher temperatures) can represent the reaction order indicating the effect of the unreduced



Fig. 9. Weibull plots for the reduction process of NiO in hydrogen atmosphere at different operating temperatures: ( $\blacksquare$ ) 245 °C; ( $\bigcirc$ ) 255 °C; ( $\Box$ ) 265 °C; ( $\bigcirc$ ) 275 °C and ( $\diamond$ ) 300 °C.

material on the reaction rate of the investigated process (Fig. 2). It seems that both M and N are complex functions of operating temperature, implying that both reaction orders M and N (including the reaction order n) are temperature-dependent, not constants.

Fig. 9 shows the Weibull plots (Eq. (9)) obtained for reduction process of NiO samples at the isothermal operating temperatures of 245, 255, 265, 275 and 300 °C (the location parameter ( $\gamma$ ) for all considered temperatures is equal to zero).

The approximately linear relationship is satisfied in a wide range of  $\alpha$  values and in all five cases the linear correlation coefficient (r) is higher than 0.9945.

The obtained values of Weibull distribution parameters ( $\beta$  and  $\eta$ ) and values of rate constants (1/ $\eta$ ) for reduction process of NiO at 245, 255, 265, 275 and 300 °C are shown in Table 6.

The obtained values of the shape parameter ( $\beta$ ) decreases with increase in temperature from 245 to 275 °C and then slightly increases from 275 to 300 °C. On the other hand, scale parameter ( $\eta$ ) decreases with the increase in temperature. The obtained values of rate constant ( $1/\eta$ ) show an increase in trend with temperature (Table 6). The dependence of shape parameter ( $\beta$ ) on the temperature (*T*) can be described by the polynomial function:

$$\beta = a + bT + cT^2 + dT^3,$$
(18)

where a = 11.766, b = 0.025 (°C)<sup>-1</sup>,  $c = -5.873 \times 10^{-4}$ (°C)<sup>-2</sup> and  $d = 1.280 \times 10^{-6}$  (°C)<sup>-3</sup> are corresponding 2242

#### Table 6

The linear domains of  $\alpha$  ( $\Delta \alpha$ ), the parameters  $\beta$  and  $\eta$  of the Weibull distribution function as well as the values of  $1/\eta$  (rate constant) with  $\gamma$  equal to zero, obtained by Weibull plot method for reduction process of NiO using hydrogen at five operating temperatures

Temperature (°C)	Δα	β	$\eta$ (min)	$1/\eta \ (min^{-1})$	r <sup>a</sup>	$SD^b$
245	0.10-0.95	1.40	47.62	0.0210	0.9956	0.0763
255	0.12-0.95	1.06	25.32	0.0395	0.9957	0.0681
265	0.14-0.95	0.94	15.29	0.0654	0.9996	0.0207
275	0.14-0.95	0.74	9.51	0.1051	0.9955	0.0629
300	0.17-0.95	0.88	5.79	0.1726	0.9978	0.0496

<sup>a</sup>Linear correlation coefficient.

<sup>b</sup>Standard deviation.

#### Table 7

The values of Weibull distribution parameters obtained by non-linear curve fitting  $(\beta_{NL}, \eta_{NL})$  for  $\alpha \in (0,1)$  and by maximum likelihood (ML) method  $(\beta_{ML}, \eta_{ML})$  (Eqs. (10) and (11)10,11) at five different operating temperatures 245, 255, 265, 275 and 300 °C

Temperature (°C)	$\beta_{NL}$	$\eta_{NL}$ (min)	$\beta_{ML}{}^{a}$	$\eta_{ML} \ (\min)^a$	Reduced Chi-sqr <sup>l</sup>
245	1.41	45.87	1.42	46.17	$1.8 \times 10^{-6}$
255	1.09	24.63	1.10	25.05	$2.3 \times 10^{-5}$
265	0.91	16.95	0.95	17.15	$2.0 \times 10^{-5}$
275	0.71	9.53	0.77	9.73	$2.0 \times 10^{-4}$
300	0.87	5.81	0.85	5.93	$9.0 \times 10^{-5}$

<sup>a</sup>Weibull parameters with 95% confidence limit.

<sup>b</sup>For non-linear curve fitting.

constants necessary to describe the relationship between mentioned parameter and temperature.

Table 7 shows the results of Weibull distribution parameters  $(\beta, \eta)$  obtained by direct non-linear curve fitting of experimental  $\alpha(t)$  plots (Fig. 1) on the cumulative Weibull distribution function and by the ML method (Eqs. (10) and (11)). The non-linear curve fitting of experimental  $\alpha(t)$  plots were performed in the whole range of the fractional extent of reaction ( $\alpha \in (0,1)$ ) at all considered temperatures.

From Table 7 it can be seen that the obtained values of Weibull distribution parameters calculated by non-linear curve fitting of experimental  $\alpha(t)$  plots and by ML method are in good agreement with values of Weibull parameters obtained by the Weibull plot method (Table 6).

Figs. 10 and 11 show the comparison of experimental rate-time curves (symbols) and Arrhenius-Weibull probability density functions (full lines) (Eq. (13)) for the reduction process of NiO using hydrogen at 245 and 275 °C. For calculating the Arrhenius-Weibull probability density functions, the different values of shape parameter ( $\beta$ ) (Table 6), the average value of apparent activation energy ( $E_a$ ) obtained by isoconversional method in the 0.30 <  $\alpha$  < 0.70 range, and the average values of pre-exponential factors from Tables 4 and 5 were used.



Fig. 10. Comparison of experimental rate–time curve (symbol ( $\Box$ )) and Arrhenius–Weibull probability density function (full line) (Eq. (13)) for reduction process of NiO using hydrogen at T = 245 °C.



Fig. 11. Comparison of experimental rate–time curve (symbol ( $\bigcirc$ )) and Arrhenius–Weibull probability density function (full line) (Eq. (13)) for reduction process of NiO using hydrogen at T = 275 °C.

From Figs. 10 and 11 it can be seen that the Arrhenius–Weibull probability density functions very well describe the experimental rate–time curves for calculated Weibull shape parameters ( $\beta$ ) at 245 and 275 °C (Table 6).

If  $\beta$  is greater than 1 the rate of process increases with *t*, whereas if  $\beta$  is less than 1 the rate of process decreases with *t*. This statement confirms the results presented in Figs. 2, 10 and 11. From the results given above we conclude that  $\beta$  parameter should be a behaviour index indicating the kinetic pattern of the mechanism controlling the process studied. Also, from the above results, it follows that the rate-limiting step under the same reaction mechanism of the considered process probably change with operating temperature.

From isoconversional dependence of reaction times on the apparent activation energies ( $t_{|\alpha} = f(E_a)$ , Fig. 12), the mathematical relationship between the time and apparent activation energy can be evaluated.

The numerically evaluated relation between the time (t) and the apparent activation energy  $(E_a)$  is given by the expression

$$t = \tau \exp(\varepsilon E_a),\tag{19}$$

where  $\tau$  and  $\varepsilon$  are the fitting coefficients. The coefficient  $\tau$  has the dimension of time, whereas  $\varepsilon$  has the dimension mol kJ<sup>-1</sup>. The coefficient  $\tau$  represents the "solid" constant and does not have any physical meaning. On the other hand, the coefficient  $\varepsilon$  represents the exponential constant in Eq. (19) and has a role as numerical correction term for isoconversional dependence of reaction times (*t*) on apparent activation energies (*E<sub>a</sub>*).



Fig. 12. The isoconversional dependence of reaction times (t) on the apparent activation energies ( $E_a$ ) for the reduction process of NiO in hydrogen atmosphere at different operating temperatures (lines represent the B-Spline curves which show the trends of reaction time values (symbols) with progress of apparent activation energy values).

## Table 8

The influence of operatin	ng temperature on th	ne values of fitting	g coefficients
$(\tau \text{ and } \varepsilon)$ , for reduction	process of NiO in h	ydrogen atmosph	nere

τ (min)	$ \epsilon  \; (mol  kJ^{-1})$
$1461.49 \pm 235.33$	$0.0395 \pm 0.0020$
$1866.46 \pm 485.80$	$0.0479 \pm 0.0034$
$1167.96 \pm 220.25$	$0.0466 \pm 0.0025$
$1629.31 \pm 527.72$	$0.0541 \pm 0.0043$
$1703.79 \pm 433.94$	$0.0638 \pm 0.0034$
	r (min) 1461.49±235.33 1866.46±485.80 1167.96±220.25 1629.31±527.72 1703.79±433.94

The influence of isothermal operating temperatures (*T*) on the values of fitting coefficients ( $\tau$  and  $\varepsilon$ ) is shown in Table 8.

The values of fitting coefficients  $\tau$  and  $\varepsilon$  increase with increase in temperature from 245 to 255 °C. In the temperature range  $255 \le T \le 265$  °C, the fitting coefficients ( $\tau$  and  $\varepsilon$ ) decreased. In addition, from 265 to 300 °C, the considered fitting coefficients increase again. The time dependence of apparent activation energies can appear in very complex reaction systems or in a simple system where there is an energy distribution of active centres. From such dependence (Fig. 12), we can evaluate the ddf of activation energies at different experimental temperatures. The ddf of apparent activation energies ( $g(E_a) = d\alpha/dE_a$ ) can be obtained from Eq. (12) and the following relation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}E_a} = \frac{\mathrm{d}\alpha}{\mathrm{d}t} \times \left| \frac{\mathrm{d}t}{\mathrm{d}E_a} \right|. \tag{20}$$

From Eq. (19) we can easily obtain the following expression:

$$\left|\frac{\mathrm{d}t}{\mathrm{d}E_a}\right| = \tau\varepsilon \exp(\varepsilon E_a). \tag{21}$$

The distribution function  $g(E_a) = d\alpha/dE_a$  is now given in the form:

$$g(E_a) = \frac{\beta \tau \varepsilon \exp(\varepsilon E_a)}{\eta} \left( \frac{\tau \exp(\varepsilon E_a)}{\eta} \right)^{\beta-1} \\ \times \exp\left[ -\left( \frac{\tau \exp(\varepsilon E_a)}{\eta} \right)^{\beta} \right].$$
(22)

The influence of isothermal operating temperatures on the shape of ddf of the apparent activation energies is shown in Fig. 13.

The basic characteristics of the ddf of apparent activation energies the following:  $E_{a,max}$ —the value of apparent activation energy at the maximal value of distribution function,  $g(E_a)_{max}$ —the maximal value of ddf,  $g(E_a)_{HW}$  the value of ddf on the half-wide, SF—shape factor or factor of asymmetry.HW: half-width of the ddf, at different experimental temperatures, are presented in Table 9.

From results in Table 9 and Fig. 13, we note that following observations exist: (a) the values of  $E_{a,max}$  increase with increase in temperature and they approach the average value of the apparent activation energy

obtained by isoconversional method in the restricted interval  $0.30 < \alpha < 0.70$ , (b) the intensity of distribution functions decrease with increase in temperature, (c) the shape factors vary with the temperature, and (d) the width of ddfs increase with increase in temperature (HW, Table 9).

From the results given above it follows that at lower temperatures (245 and 255 °C) the ddfs (for  $\beta > 1$ ) are narrower and displaced to lower values of apparent activation energy. Against this, at higher temperatures (at T > 255 °C), the ddfs (for  $\beta < 1$ ) are wide and displaced to higher values of apparent activation energy. Changes of this kind, which are presented on the ddfs, can indicate the changes in rate-limiting step with temperature.

From the isoconversional behaviour of  $E_a$  on  $\alpha$  (Fig. 4a) we can conclude that reduction process considered can be described by the sequential reaction model [40] in which rate-limiting step can change conversion level as temperature changes. In fact, for the sequential reaction model, the value of apparent activation energy of the initial step



Fig. 13. The influence of operating temperature on the shape of ddfs of activation energies  $(g(E_a)$  was calculated from Eq. (22)), for reduction process of NiO in hydrogen atmosphere.

(nucleation process) is higher than the value of apparent activation energy of the following step (growth process) (see Fig. 4a). Furthermore, at lower temperatures  $(T \leq 255 \,^{\circ}\text{C})$ , the initial step (nucleation) is rate limiting, and sigmoidal behaviour of  $\alpha - t$  curves is observed (Fig. 1). On the other hand, at higher temperatures ( $T \ge 265 \,^{\circ}$ C), the following steps (growth of nuclei and theirs propagation) become rate limiting and in that case, the deceleratory behaviour of  $\alpha - t$  curves is observed (Fig. 1). For the considered NiO reduction process, probably at lower temperatures we have less number of nucleation sites which grow and eventually merge. In the high-temperature regime, the reaction surface is probably quickly saturated with nucleation sites and one goes almost simultaneously into a diffusional reaction through a layer of reduced Ni atoms. The values of Šestak-Berggren kinetic parameters (M, N) and values of the apparent reaction order (n) for the global kinetic analysis of the reduction process correspond to the following mechanism: instantaneous nucleation (saturation of the sites capable of nucleation prior to the process) and subsequent three-dimensional growth of the nuclei by diffusion controlled rate [20,41].

For the complex reduction process, the reaction model can be presented by adding both autocatalytic and nth order terms, and the expression for overall reaction rate takes the following form:

$$\frac{d\alpha}{dt}\Big]_{overall} = \underbrace{\sum_{i}^{2} k_{a}(T_{i})\alpha_{i}^{M_{i}}(1-\alpha_{i})^{N_{i}}}_{\text{Lower temperatures } T \leqslant 255 \,^{\circ}\text{C}} + \underbrace{\sum_{j}^{3} k_{b}(T_{j})(1-\alpha_{j})^{n_{j}}}_{\text{Higher temperatures } T \leqslant 265 \,^{\circ}\text{C}},$$
(23)

where subscripts *i* and *j* designate values related to a given operating temperature.  $k_a$  and  $k_b$  represent the specific autocatalytic and the *n*th order rate constant, respectively, and  $M_i$ ,  $N_i$  and  $n_j$  are the respective reaction orders. In the above Eq. (23), the influence of the reaction products on the reaction rate is given by the term  $k_a(T_i)\alpha_i^{M_i}$ . The specific rate constants ( $k_a$  and  $k_b$ ) can be obtained from the linear relationships  $(d\alpha/dt)_i = k_a f_i(\alpha_i)$  and  $(d\alpha/dt)_j = k_b f_j(\alpha_j)$ . The specific rate constants are assayed at various operating temperatures and the Arrhenius plots ( $\ln k = f[(1/T)]$ ) were used to determine the Arrhenius kinetic parameters

Table 9

The influence of operating temperature (T) on the basic characteristics of the density distribution function (ddf) of apparent activation energies,  $g(E_a)$ , for reduction process of NiO in hydrogen atmosphere

<i>T</i> (°C)	$E_{a,max}$ (kJ mol <sup>-1</sup> )	$g(E_a)_{max} \pmod{\mathrm{kJ}^{-1}}$	$g(E_a)_{HW} (\mathrm{mol}\mathrm{kJ}^{-1})$	Shape factor, SF	Half-wide, HW (kJ mol <sup>-1</sup> )
245	86.6	0.0204	0.0141	0.7377	31.8
255	89.5	0.0193	0.0134	0.7330	33.1
265	93.5	0.0161	0.0111	0.7807	40.6
275	95.4	0.0147	0.0106	0.7759	41.2
300	99.4	0.0126	0.0092	0.7398	46.8

Table 10 The values of specific rate constants  $(k_a, k_b)$  and kinetic parameters  $(\ln A, E_a)$  for the multistep model (Eq. (23)) of NiO reduction by hydrogen at different operating temperatures

	$T(^{\circ}C)$	$k_a (\mathrm{min}^{-1})$	$k_b (\min^{-1})$	$E_a (\mathrm{kJmol}^{-1})$	ln A
Autocatalytic	245 255	0.0321 0.0615	_	148.0	30.92
<i>n</i> th order	265 275 300		0.0695 0.1047 0.2030	76.9	14.55

 $(\ln A \text{ and } E_a)$  for the various reaction steps in the previously introduced multistep reaction mechanism.

Table 10 shows the values of specific rate constants  $(k_a, k_b)$  and kinetic parameters  $(\ln A \text{ and } E_a)$  calculated by the kinetic procedure described above for the multistep reaction model (Eq. (23)).

From the results obtained in Table 10, it can be seen that the value of specific rate constant  $k_a$  is a much lower than the value of specific rate constant  $k_b$ . Also, the calculated apparent activation energies ( $E_a$ 's) and the pre-exponential factors (ln A) correspond to the two kinetic paths (autocatalytic and *n*th order). The value of apparent activation energy for the autocatalytic reaction step is much higher than the value of apparent activation energy for the *n*th-order reaction step (148.0 and 76.9 kJ mol<sup>-1</sup>, respectively). The obtained results are in agreement with evaluated isoconversional dependence  $E_a$  on  $\alpha$  (decreasing dependence of  $E_a$  on  $\alpha$ , from  $E_a = 155.2$  kJ mol<sup>-1</sup> (for  $\alpha = 0.05$ ) to the  $E_a = 70.4$  kJ mol<sup>-1</sup> (for  $\alpha = 0.95$ )) which corresponds to a sequential reaction mechanism.

To visualize the above phenomenon clearly, the reaction rate is plotted as a function of conversion at different operating temperatures in Fig. 14. Fig. 14 shows comparison of experimental data for investigated reduction process and model-fitted results of sequantial model (Eq. (23)).

It is shown that the reduction process proceeds through an autocatalytic kinetic mechanism first, and then is followed by an *n*th-order one, where the reaction rate increases with increase in operating temperature. From Fig. 14, it is clear that at the lower operating temperatures, the reaction rate increases up to a maximum value, indicating again that the autocatalytic phenomena occur during the early stages of the reduction process. It can be seen that the predicted values matched the experimental data very well. However, it should be pointed out that at higher operating temperatures (separately at 300 °C) for the latter stage of the reaction ( $\alpha > 0.80$ ), the data from the sequential model show the deviation from the experimental results. These results show that a deviation of the prediction of the original model will be caused if diffusion control in the latter stage of the reaction is not properly considered. Because of this fact, the diffusion effect at higher temperatures probably has important influence on the reduction kinetics. At low temperature, the reaction



Fig. 14. Curves of reaction rate vs. conversion with model predictions for reduction process of NiO in hydrogen atmosphere at different operating temperatures. The solid lines represent the sequential model.

profile may be sigmoidal because of limited nucleation sites. So the geometric convergence of growing spheres may be the defining characteristic. At high temperature, the *n*th-order model is more consistent with a chemical reaction and rapid nucleation. In this case we have the reaction surface which is quickly saturated with nuclei including the faster diffusion of Ni atoms to appropriate nucleation sites, where at lower temperatures the water molecules retained on the surface retards nucleation by limiting this diffusion process.

It should be noted that the approximation of a single reaction model may suffer in general applicability because of the different apparent activation energies. With the present model, the reduction process of NiO by hydrogen under isothermal conditions can be successfully described for all operating temperatures considered.

#### 5. Conclusions

The kinetic process of the isothermal reduction of nickel oxide, obtained by sol-gel procedure using hydrogen, has been studied by conventional and Weibull kinetic analysis. The isothermal isoconversional method is used to yield the dependence of the apparent activation energy and preexponential factor of reduction process on the fractional extent of reaction ( $\alpha$ ). The obtained average value of apparent activation energy ( $E_a$ ) in the  $0.30 < \alpha < 0.70$  range is  $100.7 \text{ kJ mol}^{-1}$ . From both the kinetic procedures it is clear that at lower temperatures ( $245 \,^\circ\text{C} \leq T \leq 255 \,^\circ\text{C}$ ) a sigmoid group of kinetic models (two-parameter Šesták-Berggren (SB) autocatalytic model) hold whereas at higher temperatures  $(265 \degree \le T \le 300 \degree C)$  a deceleratory group of kinetic models (Fn kinetic model) hold.

From the results given in this paper, we may conclude that the shape parameter of Weibull distribution function  $(\beta)$  should be a behaviour index, indicating the kinetic pattern of the mechanism controlling the process studied. From the complex manner of shape factor on the temperature, we may conclude that the investigated system is sensitive to temperature changes. This fact was confirmed by the evaluated density distibution functions (ddf) of apparent activation energies whose shapes and characteristics show alterations with temperature. From the complex isoconversional behaviour of  $E_a$  on  $\alpha$ , and from the shapes of  $Y(\alpha)$  and  $Z(\alpha)$  functions, together with evaluated experimental RTPs, it is clear that the investigated reduction process can be successfully described by sequential-reaction mechanism. The  $E_a$ 's corresponding to the two reaction steps (autocatalytic and nth order) are obtained (148.0 and 76.9 kJ mol<sup>-1</sup>) from the Arrhenius plots of  $\ln k$  vs. 1/T, with the specific rate constants ( $k_a$  and  $k_b$ ) obtained from the proposed model.

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