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Autocatalytic Effect in the Processes of Metal Oxide Reduction.
I. Kinetic Model of the Reduction

JERZY SŁOCZYŃSKI AND WALDEMAR BOBIŃSKI

Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, ul. Niezapominańazek, 30-239 Kraków, Poland

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Kinetic analysis of a model of the consecutive autocatalytic reaction has been carried out and the results of this analysis have been applied to the description of reduction of transition metal oxides. The proposed model is compared with the consecutive noncatalyzed reaction and the consecutive reaction in which the second step is limited by the nucleation process. It is shown that different mechanisms of the reduction can be distinguished on the kinetic bases. © 1991 Academic Press, Inc.

1. Introduction

Processes of metal oxide reduction by gaseous reductants have been extensively studied due to both their practical applications and their importance in the developement of the theory of solid state reactions. Kinetics of many heterogenous reactions have been described by Delmon (*1*) and Barret (*2*). A comprehensive review of the research on the reduction of transition metal oxides has been given by Haber (*3*).

The majority of the authors have observed a sigmoidal change in the degree of reduction, α, with time, which indicates that the rate of reduction versus t or α goes through a maximum. This type of kinetics is usually explained by accepting growth of nuclei of a solid reaction product as a rate-limiting step. The acceleration of the reaction can be explained alternatively by an autocatalytic effect. This concept was introduced first in the description of reduction of cobalt molybdate by hydrogen (*4*). Recently Sloczyński (*5*), analyzing the data of Ueno *et al.* (*6*) on reduction of MoO_3 by hydrogen, has shown that the reaction kinetics may also be explained by the autocatalytic effect.

In the present paper a detailed analysis of kinetics of the consecutive autocatalytic reaction (CAR) is given; the results of this analysis are then applied to the description of transition metal oxide reduction. A proposed model is compared with the consecutive noncatalyzed reaction (CNR) as well as with the consecutive nucleation limited reaction (CNUR). In the second part of this paper the proposed model of the consecutive autocatalytic reaction is applied to the description of the reduction kinetics of MoO_3, both unsupported and deposited on various supports.

2. Results and Discussion

2.1. Formulation of a Model of the Consecutive Autocatalytic Reduction of Metal Oxides

Reduction of a metal oxide to metal or to a lower oxide is often a two-step or multistep

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process. In particular, reduction of transition metal oxides yields as a rule intermediate products in a sequence of reactions such as

$$MoO_3 \rightarrow Mo_4O_{11} \rightarrow MoO_2$$
$$V_2O_5 \rightarrow V_6O_{13} \rightarrow V_2O_4$$
$$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \text{ etc.}$$

Notwithstanding general recognition of these facts, a kinetic description in which metal oxide reduction is considered as a consecutive reaction has been lacking so far.

The reduction of a metal oxide in a reducing atmosphere, e.g., of hydrogen, or of a simple hydrocarbon, is an example of a topochemical reaction of the type: $G_1 + S_1 = G_2 + S_2$. A characteristic feature of such a reaction is its occurrence at an interface separating a solid substrate from the gas phase, or from a solid product. If desorption of gaseous products of the reduction and transport of gaseous reactants to and from the reaction interface are fast when compared to other steps of the process, the total reaction rate, measured experimentally, may be expressed as $r(p_i, T) \cdot S(t)$. The first term denotes the proper reaction rate which depends only on pressure of the reductant and on temperature. The second term $S(t)$ pertains to the size of the reaction interface which may change even considerably in the course of the reaction, for instance, when the growth of nuclei of the solid product is a rate-determining step. This case is discussed in detail in Section 5. If the nucleation is fast, grains of the substrate are immediately covered with a thin reduced layer from which crystallization of the reaction products is initiated. The reaction interface decreases with time proportionally to the nth power of the sample mass with $n = \frac{2}{3}$ for spherical grains and $n = \frac{1}{2}$ for elongated cyliders. The case $n = 1$ corresponds to the reaction involving also the volume of a sample, i.e., when the reducing gas dissolves fast in the oxide under reduction. This takes place, for instance, during reduction by hydrogen, or by hydrocarbons, which yields by dissociative adsorption atomic hydrogen that easily penetrates into the bulk of the oxide. The above model called "the shrinking core model" (*7*), with various additional modifications, has been frequently applied to the description of the reduction processes (*8–10*).

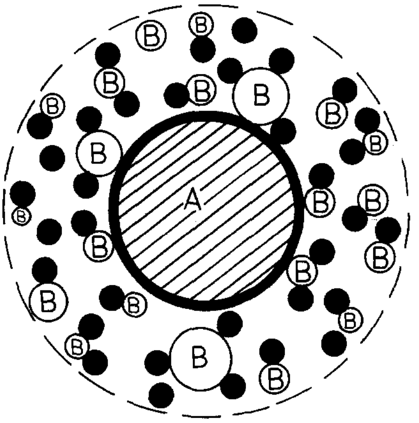


FIG. 1. Schematic representation of a substrate grain in an advanced stage of reduction. Black circles denote the final product C.

According to this model, at constant temperature and pressure of a reductant, the rate of consumption of the substrate A is proportional to the surface of unreacted grains, that is to the nth power of the actual content of the substrate A in the sample. If an intermediate product B is reduced in the same way, the rate of its reduction is also proportional to the nth power of its content in the mixture of the reactants. The situation occurring at an advanced stage of reduction is shown in Fig. 1. An initial grain of the substrate A contains numerous grains of the intermediate product B and grains of the final product C.

The autocatalytic action of product C consists most probably in facilitating a dissociative adsorption of the reductant which leads to the formation of reactive atomic hydrogen at the surface. Traces of dispersed metal, usually present in a lower oxide which is the final product of the reduction, may activate hydrogen or hydrocarbons used as the reductants. For example, small amounts of cobalt were found on reducing $CoMoO_4$ (*11*) and traces of molybdenum were identified among the products of reduction of $CoMoTeO_6$ (*12*). Catalytic activity of metal admixtures, such as platinum, palladium, and nickel, activating hydrogen in the reduction of transition metal oxides was observed by many authors (*13–15*).

An obvious condition for occurrence of the catalytic effect is the existence of contacts between grains of the catalyst C and the oxide under reduction. Thus, the autocatalytic effect should be particularly pronounced in the reduction of the intermediate product B transforming directly into the final product C, which facilitates generation of a significant number of the contacts B/C. In contrast, crystallites C do not contact the substrate A, and hence the active hydrogen transfer from C to A is not possible. The above considerations lead to the conclusion that the first step of the reduction $A \rightarrow B$ is a reaction of the order $n \leq 1$ with respect to the substrate A, whereas two parallel paths can be envisaged for the second step $B \rightarrow C$: (a) the reaction of the nth order with respect to B and (b) the autocatalytic reaction, the rate of which is proportional to contents of B and C in the reaction mixture.

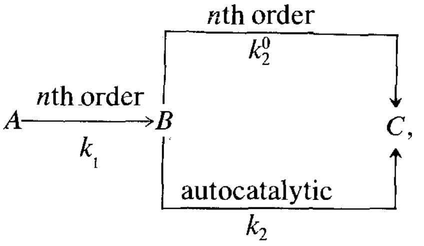
A detailed analysis of the kinetics of a reaction occurring according to the described model is given below.

2.2. *Kinetics of the Consecutive Autocatalytic Reaction*

Let us consider the reduction of a metal oxide by a gaseous reductant under constant pressure and temperature which proceeds in two consecutive steps:

$$\underset{(A)}{MO_p} \rightarrow \underset{(B)}{MO_{p\text{-}y}} \rightarrow \underset{(C)}{MO_q} \tag{2.1}$$

Let us assume that the overall reaction is described by the kinetic scheme



(2.2)

in which the first step of the reaction is of the nth order with respect to substrate A, whereas the second step is sum of the noncatalytic reaction of the nth order and the parallel autocatalytic reaction. When the contents of the solid reactants in the reaction mixtures are expressed in mole fractions, x_i, then from Eq. (2.1)

$$x_A + x_B + x_C = 1, \tag{2.3}$$

and the rates of the reaction steps are

$$-\frac{dx_A}{dt} = k_1 x_A^n \tag{2.4}$$

$$\frac{dx_B}{dt} = k_1 x_A^n - \frac{dx_C}{dt} \tag{2.5}$$

$$\frac{dx_C}{dt} = k_2^0 x_B^n + k_2 x_B^n x_C^n = k_2 x_B^n (\kappa + x_C^n). \tag{2.6}$$

Constant $\kappa = k_2^0/k_2$ gives a ratio of rate constants of noncatalyzed and autocatalyzed reactions.

The assumption that the autocatalytic reaction is accompanied by the noncatalytic reaction follows from the physical mechanism of the process, described in Section 2.1, and it is also necessary for construction of the kinetic model. Since the rate of the autocatalytic reaction is proportional to x_C, which at the onset of the reduction is zero, the reaction $B \rightarrow C$ may start only when a certain amount of the product C has been formed in a noncatalyzed reaction. Another possibility of starting up the autocatalytic reaction consists in forming a certain amount of the product C in the reaction system, e.g., by an appropriate pretreatment of the substrate A, or by addition of the autocatalyst C to the system. Hence, depending on the initial conditions, the quantity κ can be interpreted either as a ratio of the rate constants k_2^0/k_2 or as an initial content of the autocatalyst C in the mixture of the reactants.

The autocatalytic character of the second step and hence the proportionality of its rate to the content x_C gives rise to a specific hindrance of the reduction rate at the beginning of the reaction. Only when the amount of the autocatalyst C is sufficiently large does an abrupt acceleration of the process begin. Since the increase in x_C is limited and x_B decreases to zero after having reached its maximum value, the rate of reduction passes through a maximum and then decreases to zero.

As shown by Słoczyński (5) when $n = 1$, Eqs. (2.4) and (2.6) can be solved analytically. The solutions, fulfilling the initial conditions

$$x_A = 1; \quad x_B = x_C = 0 \quad \text{for } t = 0, \tag{2.7}$$

have the form

$$x_A = e^{-k_1 t} \tag{2.8}$$

$$x_c = \frac{e^{kx}}{Qx^a + \dfrac{1}{1+\kappa} - \dfrac{k^{(a+1)}}{a!}x^a \ln x + k\sum\limits_{\substack{i=1\\ i\neq a}}^{\infty} F_{ik}x^i} - \kappa \tag{2.9}$$

when a is a natural number or

$$x_c = \frac{e^{kx}}{Qx^a + \dfrac{1}{1+\kappa} + k\sum\limits_{i=1}^{\infty} F_{ik}x^i} - \kappa \tag{2.10}$$

when a is not a natural number. Constant Q is in both cases given by

$$Q = \frac{e^k}{\kappa} - \frac{1}{1+\kappa} - k\sum_{\substack{i=1\\ i\neq a}}^{\infty} F_{ik}, \tag{2.11}$$

where

$$F_{ik} = \frac{k^i}{i!(a-i)}; \quad a = (1+\kappa)k; \; k = \frac{k_2}{k_1}; \tag{2.12}$$

and x is an operational variable related to time:

$$x = e^{-k_1 t}. \tag{2.13}$$

Concentration x_B can be found from Eq. (2.3). From the preceding equations, $x \to 0$, $x_B \to 0$, $x_C \to 1$ when $t \to \infty$.

When $0 < n < 1$, the solution of Eq. (2.4), combined with conditions (2.7), is given by

$$x_A = [1 - (1-n)k_1 t]^{1/(1-n)}, \tag{2.14}$$

whereas the solution of Eq. (2.6) probably cannot be expressed by elementary functions. A numeric solution of the latter equation is given later in this work.

A significant difference in integrating the above equation for $n = 1$ and $0 < n < 1$ should be stressed at this point. In the first case, x_A decreases asymptotically to zero when $t \to \infty$, which allows the use of the operational variable $x = e^{-k_1 t}$ as the representation of time. This is not possible for $0 < n < 1$ since, as it follows from Eq. (2.14) that x_A decreases to zero after a finite time $t = 1/(1 - n)k_1$.

The case $n = 1$ has a fundamental significance for the full discussion of the kinetics of Reaction (2.2), since its analytical solution is known. A discussion of this problem presented below is based on the assumption that the kinetics of the reaction is dominated by its consecutive and autocatalytic character, whereas small changes of the reaction order at a given step are of secondary importance. The comparison carried out below for $n = 1$, $n = \frac{2}{3}$, and $n = \frac{1}{2}$ has shown that a qualitative picture of Reaction (2.2) is the same for all the cases and that the change in the order brings about small quantitative differences in the form of the function $(R/R_0)(\alpha)$.

2.3. *Application of the Model of the Consecutive Autocatalytic Reaction to Reduction of Transition Metal Oxides*

Full discussion of this question, based on the solutions of Eqs. (2.4) and (2.6) for $n = 1$, is presented below. In the final part of this section, a comparison of selected kinetic characteristics, obtained from the solutions for $n = 1$, $n = \frac{2}{3}$, and $n = \frac{1}{2}$, is given for a representative range of k and κ.

Eqs. (2.10) and (2.8) combined with relation (2.3) provide for a full kinetic analysis of the autocatalytic reaction. However, in order to verify experimentally the proposed model or to determine the rate constants from experimental data, the contents of all the solid reactants should be measured as a function of time. This is a difficult experimental task and usually studies on the reduction of metal oxides involve determination of the degree of reduction α (by following the loss of oxygen from the sample) as a function of time, or determination of the reduction rate $R = d\alpha/dt$ as a function of time or of the reduction degree α.

From Eq. (2.1), the degree of reduction may be given by

$$\alpha = \frac{yx_B + (p - q)x_C}{p - q} = \frac{1}{\delta}x_B + x_C, \quad (3.1)$$

where

$$\delta = \frac{p - q}{y}. \quad (3.2)$$

It is evident that $y < p - q$ and, hence, $\delta > 1$.

In the following considerations, measurable functions F, such as x_B, x_C, or R, describing the reaction are used. The following formulae should be used for conversion of different variables:

$$\frac{dF}{dt} = x'\frac{dF}{dx} \text{ or } \frac{dF}{dx} = \alpha'\frac{dF}{d\alpha} \text{ or } \frac{dF}{dt} = R\frac{dF}{d\alpha}. \quad (3.3)$$

Equation (2.4) gives

$$x' = \frac{dx}{dt} = -k_1x. \quad (3.3a)$$

Taking into account this result and introducing $F = x_C$ into the first of Eqs. (3.3), one obtains

$$\frac{dx_C}{dx} = -\frac{1}{k_1x}\frac{dx_C}{dt}, \quad (3.3b)$$

which combined with (2.6) gives finally

$$\frac{dx_C}{dx} = -\frac{k}{x}x_B(\kappa + x_C). \quad (3.4)$$

The relationships between the derivatives of x_B and x_C may be obtained by differentiating Eqs. (2.3) and (3.1):

$$\frac{dx_B}{dx} + \frac{dx_C}{dx} = -1, \quad \frac{1}{\delta}\frac{dx_B}{dx} + \frac{dx_C}{dx} = \alpha' \quad (3.5)$$

$$\frac{dx_B}{d\alpha} + \frac{dx_C}{d\alpha} = -\frac{1}{\alpha'}, \quad \frac{1}{\delta}\frac{dx_B}{d\alpha} + \frac{dx_C}{d\alpha} = 1. \quad (3.6)$$

From the preceding equations the derivatives can be calculated, e.g.,

$$\frac{dx_B}{d\alpha} = \frac{\delta}{1 - \delta}\left(1 + \frac{1}{\alpha'}\right) \quad (3.7)$$

$$\frac{dx_C}{d\alpha} = \frac{1}{\delta - 1}\left(\delta + \frac{1}{\alpha'}\right), \quad (3.8)$$

which give slopes of the curves $x_B(\alpha)$ and $x_C(\alpha)$.

The derivative α', important in further discussion, may be determined from relationships (3.5) by eliminating dx_B/dx. Then

$$\alpha' = -\frac{1}{\delta}\left[1 - (\delta - 1)\frac{dx_C}{dx}\right], \quad (3.9)$$

and for the CAR model α' is, from relation (3.4), given by

$$\alpha' = -\frac{x + (\delta - 1)kx_B(\kappa + x_C)}{\delta x}. \tag{3.10}$$

We can now calculate the rate of reduction:

$$R = \frac{d\alpha}{dt} = \frac{1}{\delta}\frac{dx_B}{dt} + \frac{dx_C}{dt}. \tag{3.11}$$

Taking into account Eq. (2.5) and introducing the variable x, a general expression for a two-step reaction can be obtained

$$R = \frac{1}{\delta}k_1x\left[1 - (\delta - 1)\frac{dx_C}{dx}\right]. \tag{3.12}$$

At the initial moment, $t = 0$, the rate of formation of C is zero, i.e., $dx_C/dt = 0$, and from Eq. (3.3b) $dx_C/dx = 0$.

The same result may also be obtained by direct differentiation of Eq. (2.9) or (2.10). The initial rate of reduction is then

$$R_0 = \frac{1}{\delta}k_1 \tag{3.13}$$

and a relative change of the reduction rate is

$$\frac{R}{R_0} = x\left[1 - (\delta - 1)\frac{dx_C}{dx}\right]. \tag{3.14}$$

For the consecutive autocatalytic reaction with Eq. (3.4) being taken into account, Eq. (3.14) becomes

$$\frac{R}{R_0} = x + (\delta - 1)kx_B(\kappa + x). \tag{3.15}$$

In this equation, the right side depends only on x and the parameters of the function include only dimensionless quantities: δ, characteristic of the oxide reduced, as well as k and κ, which are ratios of the rate constants for respective steps of the reaction.

To simplify the calculations in further discussions, the operational variable x is used as an independent variable. However, it should be borne in mind that if the kinetic quantities, characteristic of a given reaction, are to have physical meaning they should be given as a function of the degree of reduction α, or of t. In the authors' opinion, the most recommended way to describe the consecutive reaction is to plot the R/R_0 values as a function of α. Such plots provide information on changes of the reaction rate in the course of the reaction. They have an additional advantage of being universal in a sense that they do not depend on the absolute values of the rate constants of respective steps of the consecutive reaction, but on their relative contributions. In order to show how the rate of reduction changes in the course of the reaction a derivative is calculated:

$$\frac{1}{R_0}\frac{dR}{dx} = 1 + (\delta - 1)k\left[(\kappa + x_C)\frac{dx_B}{dx} + x_B \cdot \frac{dx_C}{dx}\right].$$

Considering Eq. (3.4) and the first of Eqs. (3.5), one obtains

$$\frac{1}{R_0}\frac{dR}{dx} = 1 + (\delta - 1)k(\kappa + x_C) \left[\frac{k}{x}x_B(\kappa + x_C - x_B) - 1\right]. \tag{3.16}$$

Dividing this derivative by α', the derivative $(1/R_0)(dR/d\alpha)$ is obtained according to Eq. (3.3). Based on the solution of Eq. (2.6) and relation (2.3) it can be stated that the right side of Eq. (3.16) is a function of only the variable x. The complex character of this relationship does not allow, however, looking for extrema of the function R/R_0 by solving the equation $dR/dx = 0$ and discussing generally the properties of this function. The extrema of the function R/R_0 may be, however, evidenced by making use of the limit values of the derivatives dR/dx or $dR/d\alpha$ for

$$t \to 0 \Leftrightarrow \alpha \to 0 \Leftrightarrow x \to 1$$

and

$$t \to \infty \Leftrightarrow \alpha \to 1 \Leftrightarrow x \to 0,$$

i.e., the values at the beginning and the end of the reaction.

A limit for $t \to 0$ is easily found as:

$$\lim_{x\to 1} \frac{1}{R_0}\frac{dR}{dx} = 1 - (\delta - 1)k\kappa.$$

For Eq. (3.10) the limit value of the derivative is

$$\lim_{x\to 1} \alpha' = -\frac{1}{\delta}$$

and finally

$$\lim_{x\to 1} \frac{1}{R_0}\frac{dR}{d\alpha} = \delta[(\delta - 1)k\kappa - 1].$$

To calculate a limit for $x \to 0$, one should investigate the behavior of the fraction ${}^{x}B/x$, the numerator and denominator of which both approach zero. Using L'Hospital's rule we get

$$\lim_{x\to 0} \frac{x_B}{x} = \lim_{x\to 0} \frac{1 - x - x_C}{x} = -\lim_{x\to 0} \frac{dx_C}{dx} - 1.$$

To calculate a limit for the derivative dx_c/dx we make use of expression (2.10), writing it in the form

$$x_c = \frac{e^{kx}}{M} - \kappa,$$

where

$$M = Qx^a + \frac{1}{1 + \kappa} + k\sum_{i=1}^{\infty} F_{ik}x^i.$$

After differentiating,

$$\frac{dx_C}{dx} = \frac{kMe^{kx} - M'e^{kx}}{M^2}$$

$$= \frac{e^{kx}}{M^2}\bigg(kQx^a + \frac{k}{1 + \kappa} - \frac{k^2}{a - 1} - aQx^{a-1}$$

$$+ k^2\sum_{i=1}^{\infty} F_{ik}x^i - k\sum_{i=2}^{\infty} iF_{ik}x^{i-1}.$$

Let us consider two cases:

(1°) If $a < 1$, then the term containing x^{a-1} goes to infinity, and the remaining terms are constant or go to zero. Then

$$\lim_{x\to 0} \frac{dx_C}{dx} = -\infty \quad \text{and} \quad \lim_{x\to 0} \frac{x_B}{x} = \infty.$$

(2°) If $a > 1$, then all the terms containing powers of x go to zero and

$$\lim_{x\to 0} \frac{dx_C}{dx} = (1 + \kappa)^2\left[\frac{k}{1 + \kappa} - \frac{k^2}{k(1 + \kappa) - 1}\right]$$

$$= -\frac{k(1 + \kappa)}{k(1 + \kappa) - 1}$$

and

$$\lim_{x\to 0} \frac{x_B}{x} = \frac{1}{k(1 + \kappa) - 1}.$$

When $a = 1$, when using Eq. (2.9) for x_C and performing analogous calculations, it can be shown that $x_B/x \to \infty$.

The derivative of the rate of reduction can be hence written as

$$\lim_{x\to 0} \frac{1}{R_0}\frac{dR}{dx} = \begin{cases} \infty & \text{if } k(1 + \kappa) \le 1 \\ \dfrac{\delta(1 + \kappa)k - 1}{(1 + \kappa)k - 1} & \text{if } k(1 + \kappa) > 1. \end{cases}$$

The limit-values of the derivative of α' can be calculated in a similar way, and then the derivative of the rate of reduction with respect to the degree of reduction α can be obtained. Results of these calculations for the rate of reduction as well as other kinetic characteristics of the consecutive autocatalytic reaction are listed in Table I.

Using the limit values of the derivative $(1/R_0)(dR/d\alpha)$ the presence of extrema in the function R/R_0 can be discussed. As seen in Table I, for $\alpha \to 1$, the values of the derivative are always negative, whereas at the beginning of the reaction ($\alpha \to 0$) the sign of the derivative can change depending on the values of constants k and κ:

$$\lim_{x\to 0} \frac{1}{R_0}\frac{dR}{d\alpha} = \begin{cases} <0 & \text{if } k\kappa < \dfrac{1}{\delta - 1} \\ >0 & \text{if } k\kappa > \dfrac{1}{\delta - 1}. \end{cases} \tag{3.17}$$

TABLE I

Comparison of the Limit Values of Some Kinetic Quantites for the CNR, CAR, and CNUR Models

Kinetic values	Type of reaction					
	Consecutive noncatalytic reaction (CNR) $A \xrightarrow{\text{I order}} B \xrightarrow{\text{I order}} C$		Consecutive autocatalytic reaction (CAR) $A \xrightarrow{\text{I order}} B \xrightarrow[\text{autocatalysis}]{\text{I order}} C$		Consecutive nucleation (CNUR) $A \xrightarrow{\text{I order}} B \xrightarrow{\text{nucleation}} C$	
	$\alpha \to 0$	$\alpha \to 1$	$\alpha \to 0$	$\alpha \to 1$	$\alpha \to 0$	$\alpha \to 1$
$\frac{1}{R_0}\frac{dR}{d\alpha}$	$\delta[(\delta - 1)k - 1]$	$-\delta k, \quad k < 1$ $-\delta, \quad k > 1$	$\delta[(\delta - 1)k\kappa - 1]$	$-\delta k(1 + \kappa), \quad k(1 + \kappa) \le 1$ $-\delta, \; k(1 + \kappa) > 1$	$-\delta$	$-\delta$
$\frac{dx_B}{d\alpha}$	δ	$-\frac{\delta}{\delta - 1}, \quad k < 1$ $-\frac{\delta}{\delta k - 1}, \quad k > 1$	δ	$-\frac{\delta}{\delta - 1}, \quad k(1 + \kappa) \le 1$ $-\frac{\delta}{\delta k(1 + \kappa) - 1}, \quad k(1 + \kappa) > 1$	δ	0 $\left(-\frac{\delta}{\delta - 1}\right)$
$\frac{dx_C}{d\alpha}$	0	$-\frac{\delta}{\delta - 1}, \quad k < 1$ $\frac{\delta k}{\delta k - 1}, \quad k > 1$	0	$-\frac{\delta}{\delta - 1}, \quad k(1 + \kappa) \le 1$ $\frac{\delta k(1 + \kappa)}{\delta k(1 + \kappa) - 1}, \quad k(1 + \kappa) > 1$	0	1 $\left(\frac{\delta}{\delta - 1}\right)$
$\alpha' = \frac{d\alpha}{dx}$	$-\frac{1}{\delta}$	$-\infty, \quad k < 1$ $-\frac{\delta k}{\delta(k - 1)}, \quad k > 1$	$-\frac{1}{\delta}$	$-\infty, \quad k(1 + \kappa) \le 1$ $-\frac{1}{\delta}\frac{\delta k(1 + \kappa) - 1}{k(1 + \kappa) - 1}, \quad k(1 + \kappa) > 1$	$-\frac{1}{\delta}$	-1 $(-\infty)$
$\frac{x_B}{x}$	0	$\infty, \quad k < 1$ $\frac{1}{k - 1}, \quad k > 1$	0	$\infty, \quad k(1 + \kappa) \le 1$ $\frac{1}{k(1 + \kappa) - 1}, \quad k(1 + \kappa) > 1$	0	0 (∞)

In the first case, the derivative is negative at the limits of the range $\alpha \in (0, 1)$. This implies that $dR/d\alpha$ is either negative in the whole range (0, 1) or changes its sign at least twice, i.e., has at least two zero values in the range. The form of expression (3.16) does not exclude either of the two possibilities. Thus, it can be concluded that for $k\kappa < 1/(\delta - 1)$, the function R/R_0 has two extrema or that R/R_0 decreases monotonically. Physical sense demands a minimum appearing first, followed by a maximum. When $k\kappa > 1/(\delta - 1)$ the derivative of R/R_0 in the range (0, 1) goes from positive to negative values, which corresponds to a maximum in the function R/R_0.

It follows from the above discussion that three shapes of the R/R_0 vs α curves can be distinguished: (1) curves with a minimum and a maximum whereby the position of the minimum corresponds to a lower value of α when compared with position of the maximum, (2) curves with only a maximum, (3) curves with R/R_0 decreasing monotonically.

Computer simulation of the function R/R_0 illustrates the above conclusions. Figure 2 shows plots of R/R_0, x_B, and x_C for the reduction with $\delta = 4$ (e.g., $MoO_3 \rightarrow Mo_4O_{11} \rightarrow MoO_2$) and for a number of sets of values for k and κ. Three types of the curves, in keeping with criterion (3.17), can be clearly seen. The figure also demonstrates that the limit values of the slopes in the curves $(R/R_0(\alpha)$, $x_B(\alpha)$, and $x_C(\alpha)$ are in good agreement with the results given in Table I.

Finally it should be verified whether the above relationships are valid also for $0 < n < 1$, i.e., whether classification of the $(R/R_0)(\alpha)$ curves found for $n = 1$ is an immanent property of the CAR model, or whether it depends on the orders of the respective steps of the reaction.

Since, Eq. (2.6) cannot be solved analytically for $n < 1$, numerical calculations have been limited to two cases: $n = \frac{2}{3}$ (spherical grains) and $n = \frac{1}{2}$ (elongated cylindrical grains). Solutions of Eq. (2.6), for given values of k and κ, have been found using a modified Runge–Kutta method with a variable integration step (*16*). Results of the calculations are shown in Fig. 3 in the form of plots R/R_0 vs α. As one can see, the classification of the $(R/R_0)(\alpha)$ curves in three categories is valid in the range (0.1, 10) of k and κ, i.e., in the range in which the contributions of the respective steps of the reaction change a hundred times. Quantitative differences, when compared with the solutions for $n = 1$, consist of shifts of the extrema of the function $(R/R_0)(\alpha)$, and in the changes in their magnitude. For $n < 1$, the simple criterion (3.17) is no longer valid and attempts at finding a relationship determining limits of the classification of the $(R/R_0)(\alpha)$ curves have been unsuccessful.

2.4. Comparison of the Noncatalyzed Consecutive Reaction with the Consecutive Autocatalytic Reaction

Let us now analyze similarities and differences between the well known noncatalyzed consecutive reaction proceeding according to the scheme

$$A \xrightarrow[k_1]{\text{I order}} B \xrightarrow[k_2]{\text{I order}} C \qquad (4.1)$$

and the consecutive reaction with an autocatalytic step.

Kinetic analysis of Reaction (4.1) is given in textbooks of chemical kinetics and physical chemistry. The solutions are usually given in the form of relationships $x_B(t)$ and $x_C(t)$, which can be easily transformed by replacing time with the operational variable x,

$$x_B = \frac{1}{1-k}(x^k - x) \qquad (4.2)$$

$$x_C = 1 - \frac{1}{1-k}(x^k - kx), \qquad (4.3)$$

where $k = k_2/k_1$. The factor α' from Eq. (3.3) is in this case

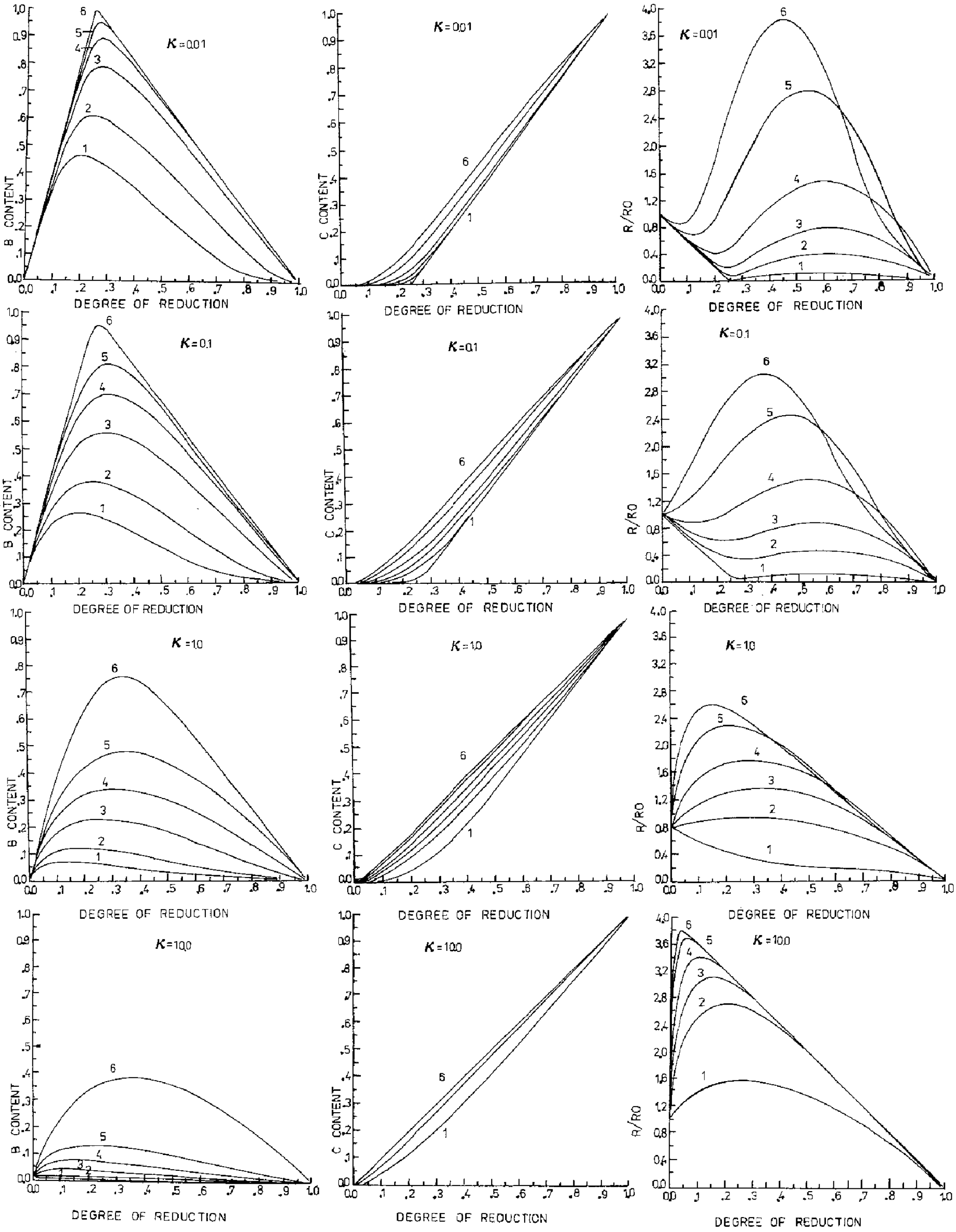


FIG. 2. Computer simulation of the kinetic curves for the CAR model, $n = 1$, $\delta = 4$. Numbers correspond to the following k values: 1, $k = 0.1$; 2, $k = 0.5$; 3, $k = 1.0$; 4, $k = 2.0$; 5, $k = 5.0$; 6, $k = 10.0$.

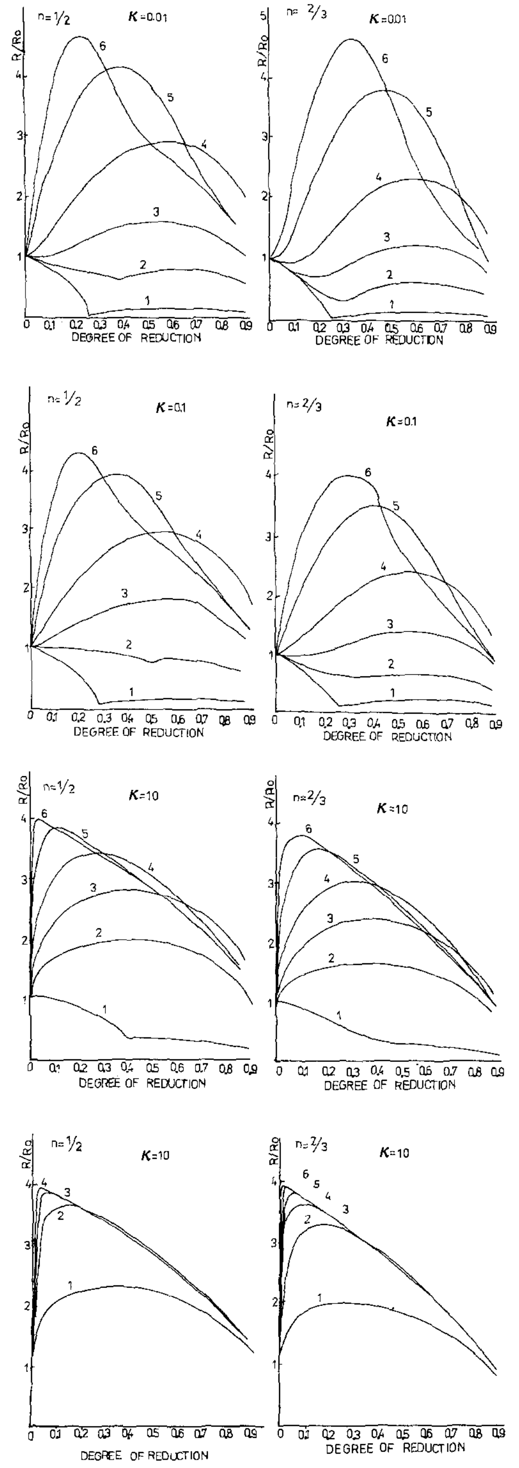


Fig. 3. Comparison of the curves $(R/R_0)(\alpha)$ of the CAR model for various values of n ($\delta = 4$).

$$\alpha' = \frac{\delta k - 1 - k(\delta - 1)x^{k-1}}{\delta(1 - k)}. \qquad (4.4)$$

Using Eq. (3.14), one can calculate a relative change in the rate of the reaction

$$\frac{R}{R_0} = \frac{1}{1-k}[(1 - k\delta)x + k(\delta - 1)x^k]. \qquad (4.5)$$

Differentiating with respect to x and multiplying the result by $1/\alpha'$, one obtains

$$\frac{1}{R_0}\frac{dR}{d\alpha} = -\delta\frac{(\delta - 1)k^2x^{k-1} + 1 - \delta k}{(\delta - 1)kx^{k-1} + 1 - \delta k}. \qquad (4.6)$$

For the reaction considered, the presence of extrema in the function R/R_0 can be directly established. It can be easily noted that the derivative (4.6) has one zero

$$x_0 = \left[\frac{\delta k - 1}{(\delta - 1)k^2}\right] \qquad (4.7)$$

which may assume the following positions depending on k

k:	$0 < k < \frac{1}{\delta}$	$\frac{1}{\delta} < k < \frac{1}{\delta - 1}$	$k > \frac{1}{\delta - 1}$
x_0:	indefinite	$x_0 > 1$	$0 < x_0 < 1$

It can be seen that the solution having physical sense exists only for $k > 1/(\delta - 1)$ and then the function R/R_0 has a maximum. When $k < 1/(\delta - 1)$, the relative rate R/R_0 decreases monotonically with the increase in α. The same conclusions can be reached when one uses the limit values of the derivative of R/R_0, as shown for the consecutive autocatalytic reaction. Using data from Table I it can be concluded that at the end of the reaction ($\alpha \cong 1$) the derivative of R/R_0 is always negative, whereas at the beginning ($\alpha \cong 0$) its sign depends on the value of k. When $k > 1/(\delta - 1)$, the derivative is positive and, hence, a maximum in the relative rate R/R_0 appears. In contrast, for $k < 1/(\delta - 1)$ the derivative is negative in the entire range $\alpha \in (0, 1)$ and the function R/R_0 decreases.

Using Eqs. (4.2), (4.3), and (4.4), derivatives, i.e., slopes of the curves $x_B(\alpha)$ and $x_C(\alpha)$, can be calculated:

$$\frac{dx_B}{d\alpha} = -\delta \frac{1 - kx^{k-1}}{\delta k - 1 - k(\delta - 1)x^{k-1}} \qquad (4.8)$$

$$\frac{dx_C}{d\alpha} = \delta k \frac{1 - kx^{k-1}}{\delta k - 1 - k(\delta - 1)x^{k-1}}. \qquad (4.9)$$

The limit values of these derivatives are given also in Table I.

Figure 4 shows R/R_0, x_B, and x_C as a function of the degree of reduction for $\delta = 4$. Two groups of the $(R/R_0)(\alpha)$ curves can be seen, one group with a maximum, and the other decreasing monotonically. It can be easily verified that the limit slopes of the curves $x_B(\alpha)$ and $x_C(\alpha)$ correspond to the values given in Table I.

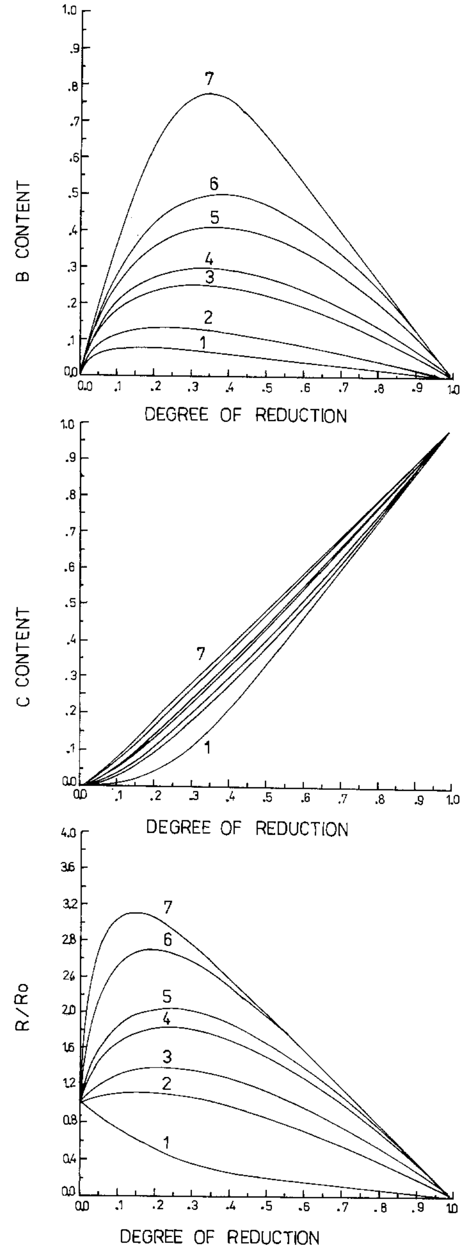


FIG. 4. Computer simulation of the kinetic curves for the CNR model ($\delta = 4$). Numbers correspond to following k values: 1, $k = 0.1$; 2, $k = 0.5$; 3, $k = 0.8$; 4, $k = 1.5$; 5, $k = 2.0$; 6, $k = 5.0$; 7, $k = 10.0$.

The above considerations indicate that in the case of the noncatalyzed consecutive reaction, the rate of reduction may either decrease monotonically with the degree of reduction or go through a maximum. If, on the other hand the reaction proceeds according to the CAR model its rate may decrease monotonically, go through a maximum, or exhibit both a minimum and a maximum in the curve $(R/R_0)(\alpha)$. Thus, the two models can be distinguished kinetically. In order to decide between the models, the experimental data could be fitted to the respective equations describing the relationship $(R/R_0)(\alpha)$ for the two cases (Eq. (3.15) or (4.5)). For a limited number of experimental results, charged with inevitable experimental errors, however, this procedure does not always lead to definite answers. In the authors' opinion a proper criterion for distinguishing the two models is provided by changes in the shape of the $(R/R_0)(\alpha)$ curves when contributions of the respective steps of the reaction to the total rate of the reduction are varied. Experiments with various reductants and with the oxide under study deposited on various supports should give different values of the rate constants of the two seps of the reaction and, hence, their contributions to the rate of reduction should be different. Changes in shape of the curves $(R/R_0)(\alpha)$ in the above experiments will point out the actual model of the reduction.

2.5. *Autocatalysis and Nucleation*

As shown in the previous sections in the course of the consecutive catalytic reaction one observes the hindering of the reduction rate at the beginning of the reaction and the abrupt acceleration of the process, after a sufficient amount of the autocatalyst C has been formed. A similar reaction course can be expected when the second stage is limited by nucleation of the product C. In this section in order to decide between these two possibilities the kinetics of the two reactions is compared.

Let us analyze a reaction proceeding according to the scheme:

$$A \xrightarrow{\text{I order}} B \xrightarrow{\text{nucleation}} C \qquad (5.1)$$

According to the Avrami–Erofeev (*2*) equation, which describes kinetics of the reaction for which growth of nuclei is a rate-limiting step, the conversion degree after time t is

$$\alpha_C = 1 - e^{-k_N t^m}, \qquad (5.2)$$

where k_N is the rate constant of nucleation and parameter m depends on the mechanism of the nucleation process. Constant k_N depends on temperature, the pressure of the reductant, and the number of nucleation sites. If nucleation involves only the surface, the number of the sites is proportional to the specific surface area of the oxide which is reduced. After differentiation and elimination of time from the right side of the equation we obtain

$$\frac{d\alpha_C}{dt} = mk_N^{1/m}(1 - \alpha)|\ln(1 - \alpha)|^{1-1/m} \qquad (5.2a)$$

or introducing $mk_N^{1/m} = k_2$ and $h = 1 - 1/m$,

$$\frac{d\alpha_C}{dt} = k_2(1 - \alpha)|\ln(1 - \alpha)|^h. \qquad (5.3)$$

To apply Eq. (5.3) to the second step of the reaction ($B \rightarrow C$), contents of the reactants must be substituted for the degree of conversion α_C. Since the degree of conversion is calculated only for the second step, this step should be treated as an independent reaction and, hence, one must assume that $x_B + x_C = 1 - x =$ constant. We can then write

$$\alpha_C = \frac{x_C}{x_B + x_C} = \frac{x_C}{1 - x} \qquad (5.3a)$$

and

$$\frac{d\alpha_C}{dt} = \frac{1}{1 - x}\frac{dx_C}{dt}.$$

Introducing the above relationship to Eq. (5.3) and substituting x for time, one obtains an equation which determines changes in the content of the product C in the course of the reaction given by scheme (5.1). This equation is analogous to expression (2.6) for the CAR model,

$$\frac{dx_C}{dx} = -k\frac{1 - x}{x}\left(1 - \frac{x_C}{1 - x}\right)\left|\ln\left(1 - \frac{x_C}{1 - x}\right)\right|^h, \qquad (5.4)$$

where $k = k_2/k_1$. The kinetics of the first step of reaction is described by Eq. (2.4) and changes of x_B may be calculated from relationship (2.3).

For $h = 0$, the Avrami–Erofeev equation reduces to the first-order equation and expression (5.4) becomes identical with the kinetic equation in the CNR model. It appears that the solution of Eq. (5.4) cannot be expressed in terms of elementary functions. A simple numeric solution based on an approximate analytical equation can be, however, proposed. Introducing

$$u = \frac{x_C}{1 - x}, \tag{5.5}$$

Eq. (5.4) becomes

$$\frac{du}{dx} - u = -k\frac{1 + x}{x}(1 - u)|\ln(1 - u)|^h. \tag{5.6}$$

Neglecting u on the left side, one obtains an equation with separated variables which, after integration, gives

$$x_c = (1 - x)(1 - e^{-\varphi}), \tag{5.7}$$

where

$$\varphi = [\ln x^{-k(1-h)}]^{1/(1-h)}. \tag{5.8}$$

Relationship (5.7), for small x, gives

$$x_C = 1 - e^{-\varphi},$$

which is the limiting solution of Eq. (5.4) for $x \ll 1$.

The numerical solution is based on the relationship

$$x_C = f \cdot (1 - x)(1 - e^{-\varphi}) \tag{5.9}$$

$$\frac{dx_C}{dx} = -f \cdot (k\frac{1 - x}{x}\varphi^h e^{-\varphi} - e^{-\varphi} + 1). \tag{5.10}$$

The factor f for a given x can be found from the condition

$$f \cdot \left(k\frac{1 - x}{x}\varphi^h e^{-\varphi} - e^{-\varphi} + 1\right) - k\frac{1-x}{x}\left(1 - \frac{x_C}{1-x}\right)\left|\ln\left(1 - \frac{x_C}{1-x}\right)\right|^h = 0, \tag{5.11}$$

assuming that f is constant in the near vicinity of x. In reality, f is a function of x which can be defined only as a set of numerical values obtained from condition (5.11). The calculations performed for a number of values of k and for various h have shown that values of f lie in the range (0.4, 1) and $f \rightarrow 1$ when $x \rightarrow 0$.

Despite the lack of an analytical form for the solution of Eq. (5.4), one can discuss the shape of the function R/R_0, on the basis of the limit values of the derivative $(1/R_0)(dR/d\alpha)$, as was the case for the CNR and CAR models. Substituting (5.4) into Eq. (3.12), one obtains

$$\frac{R}{R_0} = x\left[1 + (\delta - 1)k\frac{1 - x}{x}\left(1 - \frac{x_C}{1 - x}\right)\left|\ln\left(1 - \frac{x_C}{1 - x}\right)\right|^h\right], \tag{5.12}$$

and after differentiating,

$$\frac{1}{R_0}\frac{dR}{dx} = 1 + (\delta - 1)k\left[\left(1 + \frac{x_C}{1 - x}\right)\left|\ln\left(1 - \frac{x_C}{1 - x}\right)\right|^h + h\left(\frac{dx_C}{dx} + \frac{x_C}{1 - x}\right)\left|\ln\left(1 - \frac{x_C}{1 - x}\right)\right|^{h-1}\Bigg|\,\right]. \tag{5.13}$$

The limit values of the derivative dx_C/dx are necessary for further calculations. Its value is obviously zero at the beginning of the reaction. In order to calculate the limit for $\alpha \rightarrow 1$ $(x \rightarrow 0)$, one can make use of the asymptotic solution (5.10). Assuming that $\lim_{x\rightarrow 1} \mathrm{f} = 1$, one obtains

$$\lim_{x\rightarrow 1}\frac{dx_C}{dx} = -1. \tag{5.14}$$

The limit values α' can be now easily obtained from Eq. (3.9) and limits of the derivatives $dR/d\alpha$, $dx_B/d\alpha$, and $dx_C/d\alpha$ can be calculated. The results of these calculations are given in Table I.

It should be stressed at this point that because of the specific form of the expression

$$\frac{\mathrm{k}(1 - x)\varphi^h e^{-\varphi}}{x} (*)$$

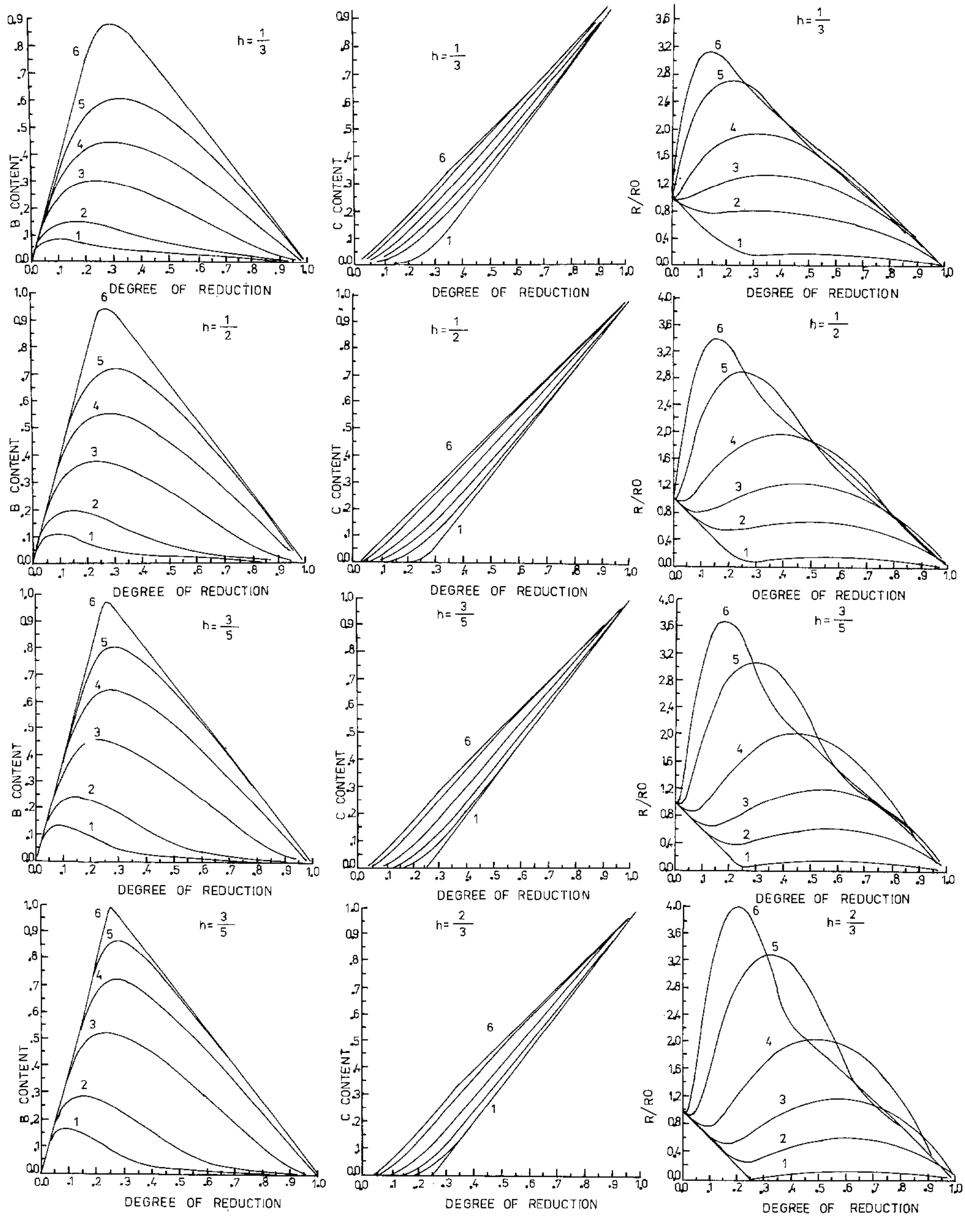


FIG. 5. Computer simulation of the kinetic curves for the CNUR model ($\delta = 4$). Numbers correspond to following k values: 1, $k = 0.1$; 2, $k = 0.5$; 3, $k = 1.0$; 4, $k = 2.0$; 5, $k = 5.0$; 6, $k = 10.0$.

the limit values are sometimes attained only in the close vicinity of 1. Generally, expression (*) goes through a maximum and, for small values of k, increases strongly with x decreasing down to α close to 1, and only then does it begin to diminish to zero. Thus, when the degree of reduction attained in experiments is not sufficiently close to 1, dx_C/dx appears to go to $-\infty$ when $\alpha \rightarrow 1$. As a consequence, apparent limit values of the other kinetic quantities are obtained. They are given in brackets in Table I. These apparent values can be observed in the plots of $x_B(\alpha)$ and $x_C(\alpha)$ shown in Fig. 4.

As to the form of the function $(R/R_0)(\alpha)$ it should be noted that in contrast to the CNR and CAR models the sign of the derivative $dR/d\alpha$ in the CNUR model is the same at the onset and at the end of the reaction, irrespective of the values of parameters k and h. This implies that the $(R/R_0)(\alpha)$ curve either decreases continuously or goes through a minimum and a maximum. Although the first possibility cannot be excluded a priori, a monotonically decreasing shape has not been obtained in the computer calculations performed for $0.1 \leq k \leq 10$ and for various h. This seems to indicate that in the CNUR model, in contrast to the CNR and CAR models, the curves $(R/R_0)(\alpha)$ are always of the same type, exhibiting a minimum and a maximum. For large values of k, the minimum can be relatively shallow and can appear at small values of α. In questionable cases, the use of the curve $(R/R_0)(t)$ should be recommended since this curve better describes the initial course of the reaction.

Figure 5 shows examples of the computer simulations of the curves $(R/R_0)(\alpha)$, $x_B(\alpha)$, and $x_C(\alpha)$ for $h = \frac{1}{3}, \frac{1}{2}, \frac{3}{5}, \frac{2}{3}$, which correspond to $m = 1.5, 2, 2.5, 3$ in the Avrami–Erofeev equation.

3. Conclusions

1. Full discussion of the considered models of reduction, based on the analytical solutions of the kinetic equations, is possible only for the CNR model, and for the CAR model when $n = 1$. Numerical methods and computer simulation must be used in the CNUR model and CAR for $0 < n < 1$.

2. Presentation of the experimental data concerning reduction of metal oxides in the form of the $(R/R_0)(\alpha)$ curves has a universal character since the shape of these curves is independent of absolute values of the rate constants of the respective reaction steps and depends only on their contributions to the total reduction process.

3. The shape of the function $(R/R_0)(\alpha)$ is different for the different models considered. In the CNR model, the rate of reduction decreases monotonically with the increasing α or it goes through a maximum. In the CAR model, in addition to the two above possibilities, a curve with a minimum and a maximum is possible. In the case of the reduction following the CNUR scheme, the $(R/R_0)(\alpha)$ curves show a minimum and a maximum.

4. Distinction between the discussed models is possible on the kinetic way by performing series of experiments with varied contributions from the respective reaction steps and analyzing the changes in the shape of the R/R_0 curves.

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