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ANOTHER APPROACH TO THE MODIFIED ZHURAVLEV EQUATION ON THE BASIS OF THE OXIDATION OF V_2O_4 AND V_6O_{13}

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Abstract

It has been found that the modified Zhuravlev equation, $[(1-\alpha)^{-1/3}-1]^2=kt^n$, which describes the kinetics of oxidation of V_2O_4 and V_6O_{13} in the temperature range 820–900 K and in the oxygen pressure range 1.0–20 kPa, can be derived via the assumption that the changes in the observed activation energy result from the changing contributions of the two diffusion processes controlling the reaction rate. The values of the observed activation energy are in the range 160–175 kJ mol^{-1} for V_2O_4 and 188–201 kJ mol^{-1} for V_6O_{13} in the scope of the experimental oxygen pressures and temperatures and conversion degrees of 0.1–0.9.

Keywords: activation energy, kinetic equation, oxidation, vanadium oxides, Zhuravlev equation

Introduction

The kinetics of oxidation of lower vanadium oxides has been discussed in several papers [1–5]. It seems that the processes of oxidation of lower vanadium oxides are controlled by diffusion and can be described by Eq. (1), derived from the Zhuravlev equation [6] with the additional assumption that the activation energy of diffusion changes during the reaction [3]:

$$\left[(1-\alpha)^{-1/3}-1\right]^2=kt^n \tag{1}$$

where α is the degree of conversion, and t is time.

Parameter k depends on temperature and oxygen pressure, and parameter n depends only on temperature. In [3], it has been assumed that the activation energy changes with time according to the following dependence:

$$\frac{\mathrm{d}E_\mathrm{a}(t)}{\mathrm{d}t}=\frac{k_\mathrm{E}}{t} \tag{2}$$

where E_a is the activation energy and k_E is a constant. Such a dependence can result from changes in a diffusion coefficient during the course of reaction, due to

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the changes in the reacting substance. Since the changes in E_a are the largest at the beginning of the reaction, dependence (2) is quite obvious. This phenomenological assumption is not related to the mechanism of diffusion.

In the present paper, another way of deriving Eq. (1) via the relation between changes in E_a and the thickness of the product layer will be presented.

Experimental

The V_2O_4 and V_6O_{13} used in the experiments were obtained by the reaction between V_2O_5 (pure for analysis) and V_2O_4 obtained by the reduction of V_2O_5 in gaseous ammonia at 1100 K. Appropriate amounts of V_2O_5 and V_2O_3 were mixed and placed in a quartz ampoule, which was heated at 890 K for 8 h and next at 1130 K for 80 h. X-ray analysis showed that the substances obtained were V_2O_4 and V_6O_{13}.

The oxidation of V_2O_4 and V_6O_{13} was carried out in a volumetric apparatus, which ensured constant temperature and constant oxygen pressure. The mass of the examined samples was about 0.150 g. A series of measurements were per-

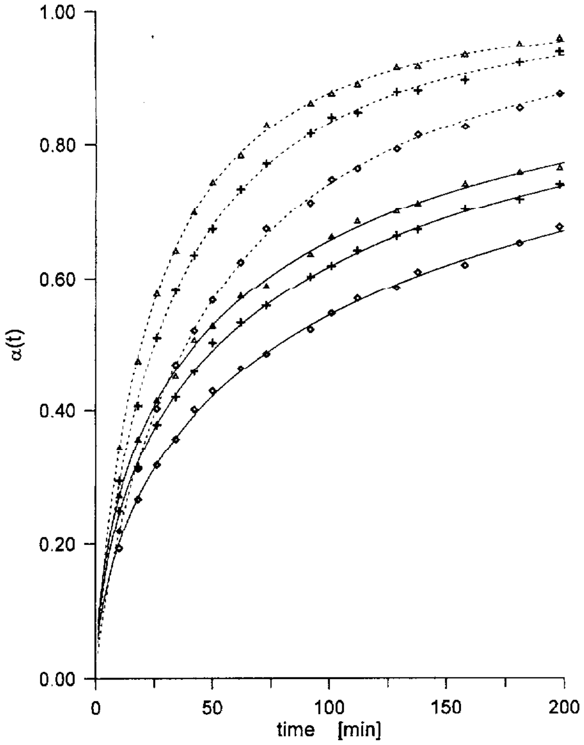

Fig. 1 α(*t*) dependence for oxidation of V_2O_4 and V_6O_{13} at an oxygen pressure of 3.4 kPa at different temperatures; (points – experimental data, lines – results of fitting; V_2O_4 – dashed line, V_6O_{13} – solid line; ◊ – 845 K, + – 872 K, △ – 890 K)

formed in the temperature range 820–900 K and in the oxygen pressure range 1.0–20 kPa.

The volume of oxygen consumed by the examined sample at every moment of the reaction was measured, and the degree of conversion, α, was determined as:

$$\alpha = \frac{V_t}{V}$$

where V_t is the volume of oxygen absorbed by the sample during time, t, and V is the volume of oxygen necessary for complete oxidation of the sample.

Results and discussion

Figure 1 depicts $\alpha(t)$ dependences at 3.4 kPa for several chosen temperatures for V_2O_4 and V_6O_{13}. Figure 2 shows $\alpha(t)$ dependences at 845 K at several chosen oxygen pressures for both examined substances as examples.

The kinetic analysis of all the obtained $\alpha(t)$ curves revealed that these curves are described with very high accuracy by Eq. (1). As Eq. (1) undergoes lineariza-

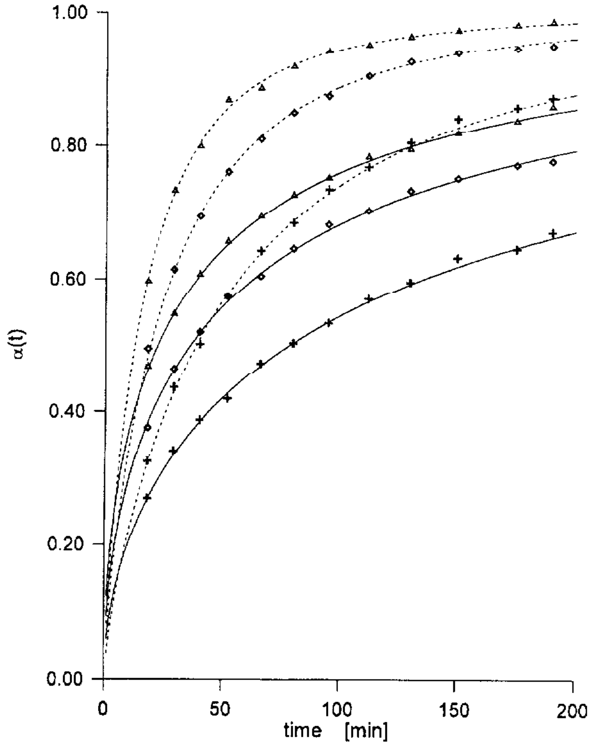

Fig. 2 $\alpha(t)$ dependence for oxidation of V_2O_4 and V_6O_{13} at 845 K at different oxygen pressures; (points – experimental data, lines – results of fitting; V_2O_4 – dashed line, V_6O_{13} – solid line; ▵ – 3.4 kPa, ◊ – 10 kPa, + – 21 kPa)

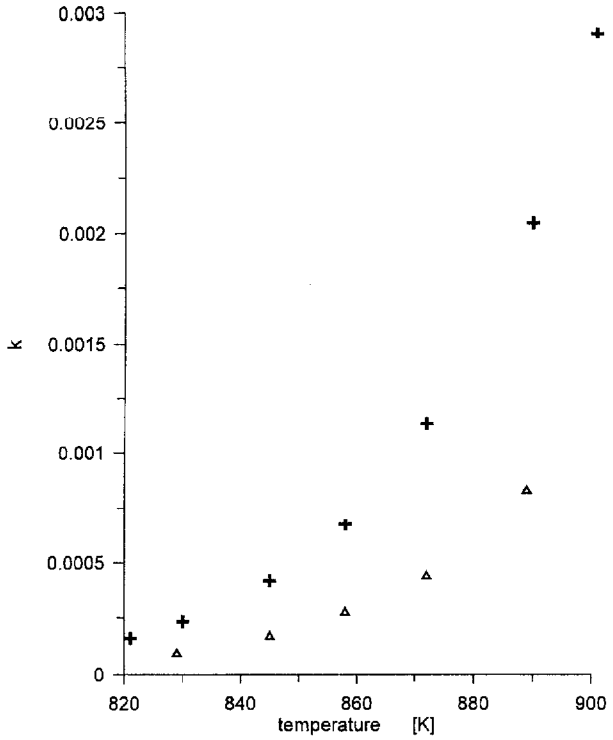

Fig. 3 Temperature dependence of parameter k in Eq. (1); (p_{O_2}=3.4 kPa; + – V_2O_4; △ – V_6O_{13})

tion, it was possible to estimate parameters k and n by the least-squares method, as the coefficients of linear regression in the system $\ln t$, $\ln[(1-\alpha)^{-1/3}-1]^2$. It was found that parameter k depends on the temperature and oxygen pressure (Figs 3 and 4), while parameter n depends only on the temperature (Figs 5 and 6).

Kinetic equation

It was assumed that, during the oxidation, the layer of V_2O_5 grows on the spherical grain of V_2O_4 as well as V_6O_{13}, and that the changes in the observed activation energy result from the changing contributions of the two diffusion processes controlling the reaction rate. It was proposed that the observed activation energy $E_a(y,T,p)$ of the overall process changes with the layer thickness according to the following dependence:

$$\frac{dE_a(y,T,p)}{dy}=\frac{k_y(T,p)}{(r-y)y}=\frac{k_y(T,p)}{r}\left(\frac{1}{r-y}+\frac{1}{y}\right) \tag{3}$$

where y is the thickness of the product layer, r is the radius of the substrate grain and k_y is a parameter dependent on temperature T and oxygen pressure p. It can be seen that $\mathrm{d}E/\mathrm{d}y$ is the sum of two factors, each of which could be related to different diffusion mechanisms.

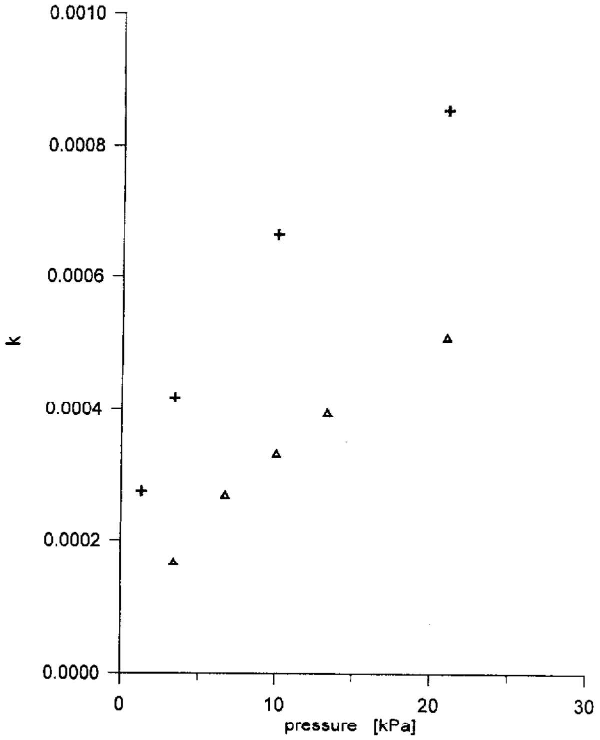

Fig. 4 Oxygen pressure dependence of parameter k Eq. (1); (T=845 K, + – V_2O_4, ▵ – V_6O_{13})

The integral form of Eq. (3) is

$$E_a(y,T,p) = E_{0.5}(T,p) + \frac{k_y(T,p)}{r}\ln\left(\frac{y}{r-y}\right) \tag{4}$$

where $E_{0.5}$ is an integration constant with the boundary condition $E_a=E_{0.5}$ for $y=0.5r$, which was introduced into the Zhuravlev kinetic equation:

$$\frac{\mathrm{d}y}{\mathrm{d}t} = k_z(T,p)\frac{1-a}{y} \tag{5}$$

where k_z is the reaction rate constant. The temperature and oxygen pressure dependence of k_z is given by the following expression based on the Arrhenius law:

$$k_z(T,p) = k_0(p)\exp\left(-\frac{E_a(y,T,p)}{RT}\right) \tag{6}$$

where $k_0(p)$ is a parameter dependent on the oxygen pressure. As a result, the following equation was obtained:

$$\frac{\mathrm{d}y}{\mathrm{d}t} = \frac{K_z}{r^3}\frac{(r-y)^{s+3}}{y^{s+1}} \tag{7}$$

where

$$K_z = k_0(p)\exp\left(-\frac{E_{0.5}(T,p)}{RT}\right) \tag{8}$$

$$s = \frac{k_y(T,p)}{rRT} \tag{9}$$

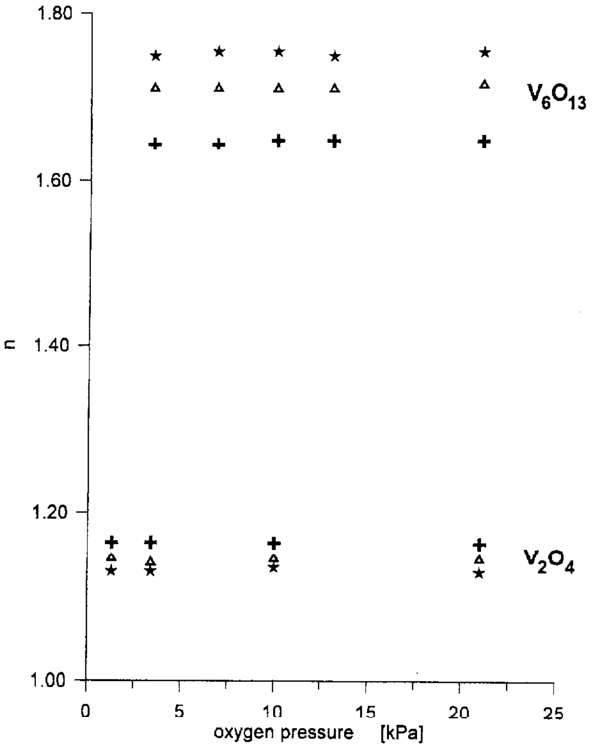

Fig. 5 Oxygen pressure dependence of parameter n in Eq. (1); (T=845 K, + – V_2O_4, ▵ – V_6O_{13})

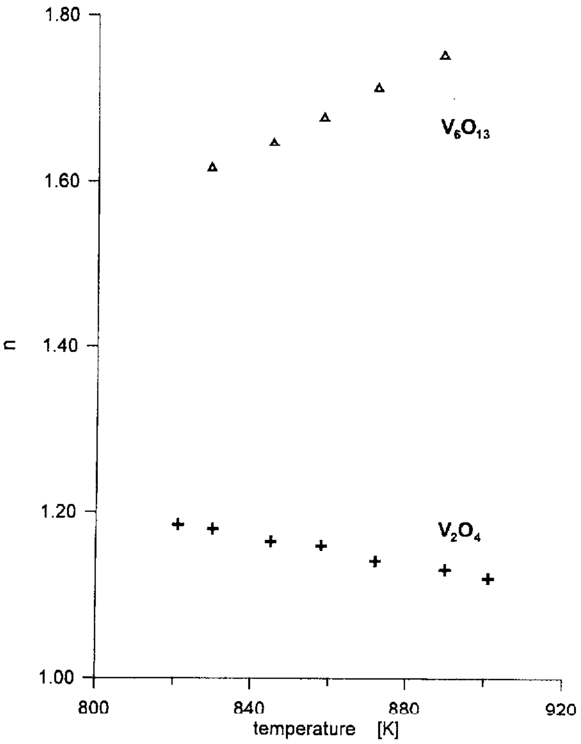

Fig. 6 Temperature dependence of parameter n in Eq. (1); (p_{O_2}=3.4 kPa, + – V_2O_4, ▵ – V_6O_{13})

After integration under the boundary condition $y=0$ for $t=0$, Eq. (7) takes the following form:

$$\left(\frac{y}{r-y}\right)^{s+2}=\frac{(s+2)K_z}{r^2}t \qquad (10)$$

and, taking into account that $\alpha=1-(1-y/r)^3$, Eq. (10) can be written as:

$$\left[(1-\alpha)^{-1/3}-1\right]^2=kt^n$$

where

$$k=\left(\frac{2K_z}{nr^2}\right)^n \qquad (11)$$

and

$$n=\frac{2}{s+2} \qquad (12)$$

Thus, it was proved that the assumption given by Eq. (3) introduced into the Zhuravlev equation (5) leads to Eq. (1).

Analysis of kinetic parameters of V_2O_4 and V_6O_{13} oxidation

The good description of the experimental α(t) curves by Eq. (1) justified the use of Eq. (4) for determination of the observed activation energies of V_2O_4 and V_6O_{13} oxidation. First, $E_{0.5}(T,p)$ and $k_y(T,p)$ for both substances have to be determined.

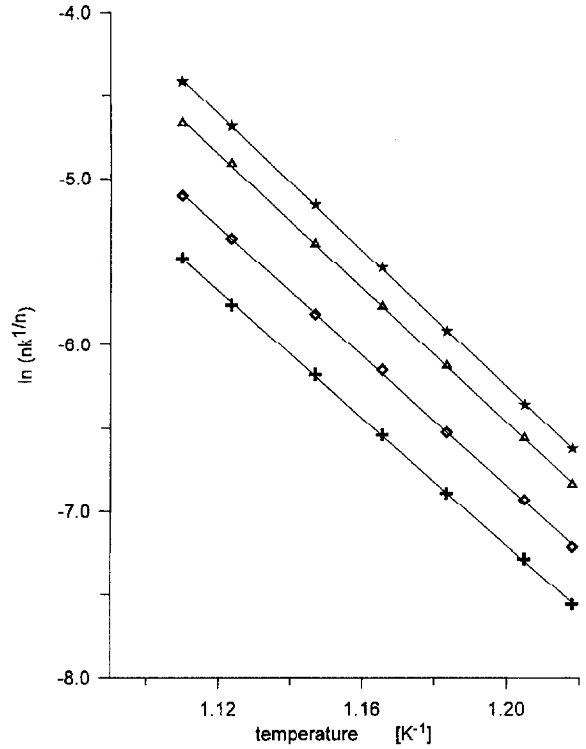

Fig. 7 Determination of $E_{0.5}$ from Eq. (13) for V_2O_4; (oxygen pressures: + – 1.3 kPa, ◊ –3.4 kPa, ▵ –10 kPa, ★– 21 kPa)

With the use of estimated values of k and n and transformed relations (11) and (12), $E_{0.5}$ can be calculated from

$$\ln(nk^{1/n}) = -\frac{E_{0.5}(T,p)}{RT} + \ln\left(\frac{r^2}{2k_0(p)}\right) \tag{13}$$

by plotting the left-hand side *vs.* $1/T$ (Figs 7 and 8 for V_2O_4 and V_6O_{13}, respectively). As a result, a straight line should be obtained with slope equal to $-E_{0.5}/R$, on the condition that $E_{0.5}$ is independent of temperature, or that this dependence

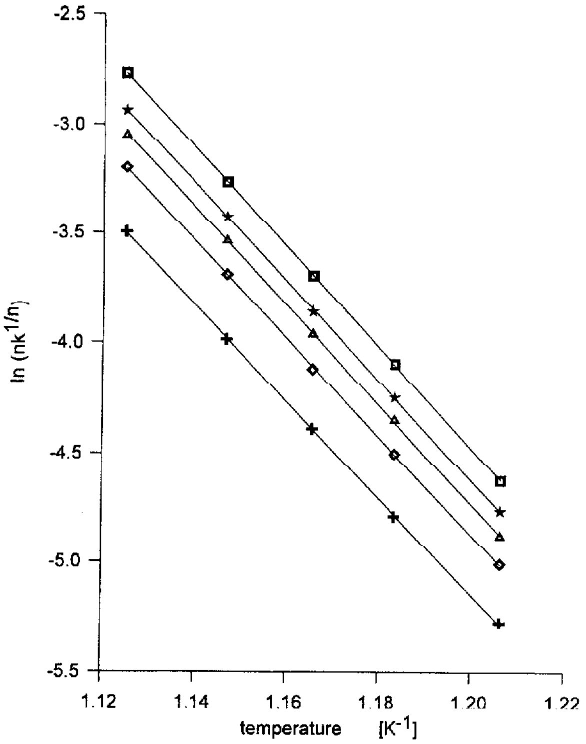

Fig. 8 Determination of $E_{0.5}$ from Eq. (13) for V_6O_{13}; (oxygen pressures: + – 3.4 kPa, ◇ – 6.8 kPa, △ – 10 kPa, ★ – 13 kPa, □ – 21 kPa)

is very weak. It is seen that for all examined oxygen pressures the temperature dependence of $E_{0.5}$ is slight, and thus $E_{0.5}(T, p) \approx E_{0.5}(p)$.

It can be demonstrated that $E_{0.5}(p)$ can be approximated by the following expressions:

for V_2O_4

$$E_{0.5}(p) = 18.4 + 1.90p^{0.16} \tag{14}$$

and for V_6O_{13}:

$$E_{0.5}(p) = 21.1 + 2.75p^{0.14} \tag{15}$$

Equation (9) combined with Eq. (12) gives the following expression for $k_y(T,p)$:

$$k_y(T,p) = 2\left(\frac{1-n}{n}\right)rRT$$

It was proved experimentally that n does not depend on the oxygen pressure (Fig. 4), so k_y depends only on temperature.

Finally, after introducing Eqs (14) and (15) into Eq. (4) and taking the relation between α and y into account, the following temperature and oxygen pressure dependences of the observed activation energies of V_2O_4 and V_6O_{13} oxidation were found:

for V_2O_4

$$E_a(\alpha,T,p) = (18.4 + 1.90p^{0.16}) + \frac{1-n}{n}RT\ln\left[(1-\alpha)^{-1/3} - 1\right]^2 \tag{16}$$

V_6O_{13}:

$$E_a(\alpha,T,p) = (21.1 + 2.75p^{0.14}) + \frac{1-n}{n}RT\ln\left[(1-\alpha)^{-1/3} - 1\right]^2 \tag{17}$$

The observed activation energy values calculated from Eqs (16) and (17) are in the range 160–175 kJ mol^{-1} for V_2O_4 and 188–201 kJ mol^{-1} for V_6O_{13}, in the scope of the experimental oxygen pressures and temperatures and the conversion degrees 0.1–0.9.

Dependences (16) and (17) expressed in a more general way can be used to interpret the observed activation energy of any process described by the modified Zhuravlev equation:

$$E_a(t,T,p) = E_{0.5} + \frac{1-n}{n}RT\ln(kt^n) \tag{18}$$

References

1 M. Taniguchi, Proc. 4th Int. Congress on Thermal Anal., Budapest, Vol. 1 (1974).
2 R. Gajerski, S. Komornicki, A. Małecki and A. Podgórecka, Mat. Chem., 4 (1979) 135.
3 A. Małecki, S. Komornicki and B. Prochowska-Klisch, Bull. Pol. Acad. Sci.: Chemistry, 29 (1981) 455.
4 A. Małecki and J. P. Doumerc, J. Thermal Anl., 31 (1986) 567.
5 A. Małecki, R. Gajerski and A. Podgórecka, Bull. Pol. Acad. Sci.: Chemistry, Part I, 35 (1987) 229, Part II, 35 (1987) 235.
6 V. F. Zhuravlev, J. G. Lasothin and R. G. Tempelman, Zh. Prikl. Khim., 21 (1948) 887.