*Journal of Thermal Analysis and Calorimetry, Vol. 76 (2004) 933–934*

*Short Communication*

# FRACTAL APPROACH IN THE KINETICS OF SOLID–GAS REACTIONS

*E. Segal*[*]

Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, Bulevardul Regina Elisabeta Nr. 4–12, Bucharest, Roumania

(Received October 31, 2003; January 27, 2004)

In our previous papers and notes [1–3], applications of fractal geometry to the solid–gas decompositions were presented. This note represents an attempt to extend the fractal approach to some existing classical data concerning the reduction with hydrogen of inorganic oxides, mainly nickel oxide [4, 5].

As far as the theoretical background is concerned, we shall extend the formula used for solid–gas decompositions according to which the total volume of the new phase at the moment $t$, $V(t)$, is given by the known relation:

$$V(t)=\int_{t_1}^{t}\left(\frac{\mathrm{d}G}{\mathrm{d}t}\right)_{\theta}\nu_{g}\,(t,\theta)\mathrm{d}\theta \tag{1}$$

where $G$ is the number of nuclei at the moment $t$, $\mathrm{d}G/\mathrm{d}t$ the rate of nucleation, $\nu_g$ the volume of a nucleus and $t_1$ the duration of the induction period. The integral from relationship (1) represents, in fact, the sum of the volumes of the nuclei which appeared when $\vartheta$ changed from $t_1$ to $t$. Actually $V(t)$ is the volume of the solid reduction product which appeared when $\vartheta$ changed in the previously mentioned range [6].

By operating in (1) the integration one obtains:

$$V(t) = k(t-t_1)^{p+q+1} \tag{2}$$

where $p$=1, 2, 3 for unidimensional, two-dimensional and tridimensional nuclei, $q= -1$for instantaneous nucleation, $q$=0 for constant rate nucleation and $q=q_s$ for a power law nucleation.

---

[*] Author for correspondence: E-mail: esegal@gw-chimie.math.unibuc.ro

*1388–6150/2004/ $ 20.00*

*Akadémiai Kiadó, Budapest*

*Kluwer Academic Publishers, Dordrecht*

As shown by Delmon there are cases of reduction of nickel oxide with hydrogen where the nuclei appear with constant rate. Under such conditions

$$\alpha^{1/4} \propto (t-t_1) \tag{3}$$

relationship satisfactory verified by the experimental data. The same experimental data are rather correctly described by means of the relation:

$$\alpha^{1/3} \propto (t-t_1) \tag{4}$$

Actually a general variant of the integral kinetic equation is

$$\alpha^{1/n} \propto (t-t_1) \tag{5}$$

with

$$3 < n < 4$$

On the other hand for the reduction of previously nucleated nickel oxide ($q$=0) with hydrogen, the experimental data are described satisfactorily either by the Eq. (5) with $n$=2 or by an equation of the same form with $n$=4.

Obviously the differences among the values of the exponent $p-q-1$ could be assigned to the rather high errors inherent to the kinetic measurements. In our opinion one has to consider as another source of non integer values of the exponent of $t$ in the kinetic equation the fractal character of the new phase nuclei. If the nuclei of the reduced phase are fractals with the fractal dimension $D$, the relationship (2) can be transcribed as:

$$\alpha(t)=k(t-t_1)^{D+q+1} \tag{6}$$

allowing for fractional values of $D$ and correspondingly fractional values of the exponent of $(t-t_1)$.

In conclusion fractality of the nuclei accounts for the previously mentioned experimental results.

Similar explanations could be advanced for the results obtained at the reduction of FeO with hydrogen [7]. After the induction period the experimental data are satisfactorily described by the kinetic law:

$$\alpha^{1/3} \propto t$$

## References

1 E. Segal, J. Thermal Anal., 52 (1998) 537.
2 E. Segal, J. Therm. Anal. Cal., 61 (2000) 979.
3 E. Segal, Rev. Roumaine Chim., 47 (2002) 701.
4 B. Delmon, Kinetika Gheteroghennykh Reaktzii, Mir, Moscow 1972, p. 77.
5 K. Hauffe, Reaktzii v tberdykh telakh i na ikh poverkhnosti, Izd. Innostrannoi Lit., Moscow 1963, p. 242.
6 P. Jacobs and F. Tompkins, Khimia Tberdovo Sostoiania, Ed. by W. E. Garner, Izd. Inostrannoi Literatury, Moskva 1961, p. 245.
7 J. Moreau, J. Bardille and J. Benard, Rev. Metallurgie, 48 (1951) 3.