Journal of Thermal Analysis and Calorimetry, Vol. 81 (2005) 145–147

FRACTAL APPROACH OF NUCLEATION IN LIQUID AND GAS PHASES

A. Dobrescu and E. I. Segal[*]

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

The authors present a generalised fractal treatment of the nucleation from the liquid solution or gas-phase reactant.

Keywords: *fractals, kinetic equation, nucleation*

Several previous notes [1–5] were dedicated to the fractals intervention in describing the reactions of the thermal decomposition of solids of the general form:

$$A_s \rightarrow B_s + C_g$$

In the kinetic equations derived by taking into consideration nucleation and nuclei growth, the fractal character of the new phase nuclei was introduced. In this note a higher generality of the gas phase or liquid phase nucleation fractal treatment is suggested. This treatment enables to describe, in principle, besides the generation of the solid product from gas phase reactants, crystallization from liquids and solutions and precipitation [6].

For the quantitative treatment the bulk disappearance of the potential nuclei which turn into real ones should be considered. Besides one has to take into account that potential nuclei can disappear due to the surface reaction as they could be incorporated by the growing nuclei [6]. One has to mention that nucleation can be normal or it can occur according to a branched chain mechanism.

For the dependence $\alpha(t)$ where α is the degree of conversion, actually for the integral kinetic equation the following equation:

$$\alpha(t) = \int_0^t (\mathrm{d}\gamma/\mathrm{d}t)_\vartheta \, v_g(t,\vartheta)\left[1-\alpha(\vartheta)\right]\mathrm{d}\vartheta \tag{1}$$

where γ represents the concentration of the nuclei, $(\mathrm{d}\gamma/\mathrm{d}t)_\vartheta$ the specific rate of nuclei generation and $v(t,\theta)$ the volume of a nucleus at the moment t, which began to grow at the moment ϑ given by:

$$v_g = \varphi k_i^p (t-\vartheta)^p \tag{2}$$

where p equals 1, 2, or 3 for uni-, bi- or tridimensional nuclei and φ is a factor which depends on the nuclei shape and the way the constant k_I (rate constant of the growth) is expressed.

For the generation of nuclei without ramification the nucleation rate takes the simple form:

$$\mathrm{d}\gamma/\mathrm{d}t = kt^q \tag{3}$$

Taking into account relations (2) and (3), equation (1) becomes:

$$\alpha(t) = A\int_0^t \vartheta^q (t-\vartheta)^p\left[1-\alpha(\vartheta)\right]\mathrm{d}\vartheta \tag{4}$$

where

$$A = \varphi k_i^p k \tag{5}$$

If the nucleation occurs with ramification, then

$$\alpha(t) = \int_0^t \left\{(\mathrm{d}\gamma_p/\mathrm{d}t)_\vartheta\left[1-\alpha(\vartheta)\right] + g_s(\vartheta)\alpha(\vartheta)\right\} v_g(t,\vartheta)\mathrm{d}\vartheta \tag{6}$$

where $\mathrm{d}\gamma_p/\mathrm{d}t$ represents the primary rate of nucleation and g_s is the secondary rate of nucleation.

$$g_s = \frac{\mathrm{d}G_s}{\mathrm{d}t} \tag{7}$$

G_s being the secondary number of nuclei.
With the substitution:

$$B(t) = 1 - \frac{g_s(t)}{\mathrm{d}\gamma_p/\mathrm{d}t} \tag{8}$$

relation (6) takes the form:

* Author for correspondence: esegal@gw-chimie.math.unibuc.ro

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

$$\alpha(t) = \mathrm{A}\int_0^t \vartheta^q (t-\vartheta)^p \left[1 - B(\vartheta)\alpha(\vartheta)\right]\mathrm{d}\vartheta \tag{9}$$

For integer values of p the literature indicates solutions of Eq. (9) based on the Laplace transform and series development [6]. Due to the fractal character of the nuclei, the exponent p could take fractional values too. In the following an attempt to solve Eq. (9) for integer and fractional values of p is presented.

In order to arrive at the general solution of the equation of Voltera type (9) we suggest the following operations [7]:

We introduce the notation:

$$\alpha(\vartheta) = \frac{! - \Phi(\vartheta)}{B} \tag{10}$$

Under such conditions from Eq. (9) we get:

$$\frac{1 - \Phi(t)}{B} = A\int_0^t \vartheta^q (t-\vartheta)^p \Phi(\vartheta)\mathrm{d}\vartheta \tag{11}$$

or

$$\Phi(t) = 1 - AB\int_0^t \vartheta^q (t-\vartheta)^p \Phi(\vartheta)\mathrm{d}\vartheta \tag{12}$$

The notation:

$$\Lambda = -AB \tag{13}$$

turns the solution of equation (12) in an obvious analytical function of Λ.

$$\Phi(t) = 1 + \Lambda\int_0^t \vartheta^q (t-\vartheta)^p \Phi(\vartheta)\mathrm{d}\vartheta \tag{14}$$

and

$$\Phi(t) = \sum_{k=0}^{\infty} \Lambda^k \Phi_k(t) \tag{15}$$

Equation (14),t aking into account the development (15) takes the form:

$$\sum_{k=0}^{\infty} \Lambda^k \Phi_k(t) = 1 + \Lambda\int_0^t \vartheta^q (t-\vartheta)^p \sum_{k=0}^{\infty} \Lambda^k \Phi_k(\vartheta)\mathrm{d}\vartheta \tag{16}$$

Thus $\Phi_0 = 1$ and

$$\Phi_k(t) = \int_0^t \vartheta^q (t-\vartheta)^p \Phi_{k-1}(\vartheta)\mathrm{d}\vartheta \tag{17}$$

The recurrence relations (17) permit an effective calculation of the values of $\Phi_k(t)$

$$\Phi_1(t) = \int_0^t \vartheta^q (t-\vartheta)^{p\Phi} \Phi_0\mathrm{d}\vartheta \tag{18}$$

or

$$\Phi_1(t) = \int_0^t \vartheta^q (t-\vartheta)^p \mathrm{d}\vartheta \tag{19}$$

The substitution

$$\vartheta = t\xi \tag{20}$$

turns Eq. (18) into:

$$\begin{aligned}\Phi_1(t) &= t^{p+q+1}\int_0^1 \xi^q (t-\xi)^p \mathrm{d}\xi = \\ &= t^{p+q+!} B(p+1,\ q+1)\end{aligned} \tag{21}$$

where

$$B(p+1,\ q+1) = \frac{\Gamma(p+1)\Gamma(q+1)}{\Gamma(p+q+2)} \tag{22}$$

$\Gamma(x)$ being the Euler function of the second kind.

$$\Gamma(x) = \int_0^{\infty} \mathrm{e}^{-t} t^{x-1}\mathrm{d}t \tag{23}$$

Similarly

$$\begin{aligned}\Phi_2(t) &= \int_0^t \vartheta^q (t-\vartheta)^p \Phi_1(\vartheta)\mathrm{d}\vartheta = \\ &= B(p+1, q+1)\int_0^t \vartheta^q (t-\vartheta)^p \vartheta^{p+q+1}\mathrm{d}\vartheta = \\ &= B(p+1, q+1)\int_0^t \vartheta^{p+2q+1} (t-\vartheta)^p\, d\vartheta\end{aligned} \tag{24}$$

Through substitution (20) we get:

$$\begin{aligned}\Phi_2(t) &= B(p+1, q+1)t^{2(p+q+1)} \\ &\int_0^1 \xi^{p+2q+1} (t-\xi)^p \mathrm{d}\xi = \\ &= B(p+1, q+1)t^{2(p+q+1)} B(p+1, 2q+p+2)\end{aligned} \tag{25}$$

or

$$\begin{aligned}\Phi_2(t) &= t^{2(p+q+1)} B(p+1, q+1) \\ &B\left[p+1, 2(q+1)+p\right]\end{aligned} \tag{26}$$

By the same procedure, for a given k we get:

$$\begin{aligned}&\Phi_3(t) = \int_0^t \vartheta^q (t-\vartheta)^p \Phi_2(t) = B(p+1, q+1)B(p+1, 2(q+1)+p) \\ &\int_0^t \vartheta^{2p+2+3q} (t-\vartheta)^p \mathrm{d}\vartheta = t^{3(p+q+1)} B(p+1, q+1)B(p+1, 2(q+1)+p)B(p+1, 3(q+1)+2p)\end{aligned} \tag{27}$$

By the same procedure, for a given k we get:

$$\Phi_k(t)=t^{k(p+q+1)}B(p+1,q+1)B(p+1,2(q+1)+p)\ldots B(p+1,k(q+1)+(k-1)p)=$$
$$=t^{k(p+q+1)}\frac{\Gamma(p+1)G(q+1)}{\Gamma(p+q+2)}\bullet\frac{\Gamma(p+1)\Gamma(2(q+1)+p)}{\Gamma(2[p+q)+3]}\ldots\ldots\frac{\Gamma(p+1)\Gamma(k(q+1)+(k-1)p)}{\Gamma[k(p+q)+k+1]} \tag{27a}$$

or

$$\Phi_k(t)=t^{k(p+q+1)}\frac{\Gamma^k(p+1)\Gamma(q+1)\Gamma(2(q+1)1+p)}{\Gamma(p+q+2)\Gamma(2(p+q)+3)}\ldots. \tag{28}$$
$$\ldots.\frac{\Gamma(k(q+1)+(k-1)p)}{\Gamma(k(p+q)+k+1)}$$

Taking into account (15), the general solution for $\Phi(t)$ is:

Correspondingly, according to (10) and (11),

$$\Phi(t)=1+\sum_{k=1}^{k=\infty}(-1)^k(ABt^{p+q+1})^k$$
$$\frac{\Gamma^k(p+1)\Gamma(q+1)}{\Gamma(p+q+2)\Gamma(2(p+q)+3)}\ldots. \tag{29}$$
$$\ldots.\frac{\Gamma(k(q+1)+(k-1)p)}{\Gamma(k(p+q)+k+1)}$$

$$\alpha(t)=\frac{1}{B}+\sum_{k=1}^{k=\infty}(-1)^{k+1}(ABt^{p1q+1})^k$$
$$\frac{\Gamma^k(p+1)\Gamma(q+1)}{\Gamma(p+q+2)\Gamma(2(p+q)+3)}\ldots. \tag{30}$$
$$\ldots.\frac{\Gamma(k(q+1)+(k-1)p)}{\Gamma(k(p+q)+k+1)}$$

For q=0 and $p\in R^+$

$$\Phi_1(t)=\int_0^t(t-\vartheta)^p\,d\vartheta=t^{p+q}B=(p+1,1)=$$
$$=t^{p+q}\frac{\Gamma(p+1)\Gamma(1)}{\Gamma(p+2)}=t^{p+q}\frac{\Gamma(p+1)}{\Gamma(p+2)} \tag{31}$$

$$\Phi_2(t)=\frac{\Gamma(p+1)}{\Gamma(p+2)}\int_0^t\vartheta^{p+1}(t-\vartheta)^p\,d\vartheta=$$
$$=\frac{\Gamma(p+1)}{\Gamma(p+2)}t^{2p+2}B(p+1,p+2)=$$
$$=t^{2p+2}\frac{\Gamma(p+1)}{\Gamma(p+2)}\frac{\Gamma(p+1)\Gamma(p+2)}{\Gamma(2p+3)}= \tag{32}$$
$$=t^{2p+2}\frac{\Gamma^2(p+1)}{\Gamma(2p+3)}$$

After k–1 iterations we get:

$$\Phi_k(t)=t^{k(p+1)}\frac{\Gamma^k(p+1)}{\Gamma(kp+k+1)} \tag{33}$$

and the general solution of $\alpha(t)$takes the form:

$$\alpha(t)=\frac{1}{B}\sum_{k=1}^{k=\infty}(-1)^{k+1}\frac{(ABt^{p+1})^k\Gamma^k(p+1)}{\Gamma(kp+k+1)} \tag{34}$$

Conclusion

A fractal approach for the for the nucleation in the liquid or gas volume of the reactants was considered. The obtained formulae for a(t) where a is the degree of conversion can be used for working the kinetic data.

References

1 R. Ozao and M. Ochiai, J. Therm. Anal. Cal., 40(1991)1331; Thermochim. Acta, 198 (1992) 279.
2 E. Segal, J. Therm. Anal. Cal., 52 (1998) 537.
3 E. Segal, J. Therm. Anal. Cal., 61 (2000) 979.
4 E. Segal, Rev. Roumaine Chim., 47 (2002) 701.
5 E. Segal, J. Therm. Anal. Cal., 76 (2004) 933.
6 B. Delmon,'Introduction a la cinetique a la cinetique heterogene', Technip, Paris, 1969, Chapter 9.
7 E. Janke and F. Emde, 'Tablitzy funktzii s formulami i krivymi', Gosudarsvennoe Izdatelstvo Fiziko-Matematitcheskoi Literatury, Moskva, 1969.

Received: July 14, 2004
In revised form: September 1, 2004

DOI: 10.1007/s10973-005-6514-1