Thermochimica Acta, 171 (1990) 87–94
Elsevier Science Publishers B.V., Amsterdam

NEW FORMAL RELATIONSHIPS TO DESCRIBE THE KINETICS OF CRYSTALLIZATION

E. URBANOVICI

Research Institute for Electrotechnics, Sfîntu Gheorghe Branch, Str. Jozsef Attila Nr. 4, Sfîntu Gheorghe, Judeţul Covasna (Romania)

E. SEGAL

Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, Bulevardul Republicii 13, Bucharest (Romania)

(Received 26 March 1990)

ABSTRACT

This work is concerned with some new formal relationships between α_{ex} and α, which describe the process of crystallization. Besides Avrami's relationship $\alpha_{ex} = -\ln(1-\alpha)$, relationships of the general form

$$\alpha_{ex} = \frac{(1-\alpha)^{1-r} - 1}{r-1} \qquad (r > 0)$$

are also considered. The values of α_{max}, corresponding to the maximum crystallization rate, calculated from these relationships are compared with the experimental values.

INTRODUCTION

Thermal methods of analysis have been applied to investigate the kinetics of crystallization. Two main types of kinetic equations were used, namely, the JMAYK [1] and Šesták–Berggren [2,3] equations, with $f(\alpha) = \alpha^m(1-\alpha)^n$.

In this paper, in order to obtain new kinetic equations to describe the crystallization process, new relationships between α and α_{ex} will be considered.

GENERALITIES CONCERNING THE PROBLEM

Two degrees of conversion have been introduced in the kinetics of crystallization, namely: α, the true degree of conversion, which describes the crystallization taking into account that the growing nuclei meet and overlap during their growth, and α_{ex}, the extended degree of conversion which describes the crystallization in an idealised way without taking into account the overlap of the growing nuclei.

In the following, according to Kemény and Šesták [1], we shall use the relationship

$$\alpha_{ex} = \left\{ \int_0^t k[T(y)] \, dy \right\}^n \tag{1}$$

where t is the time, $k(T)$ is a formal kinetic constant whose meaning is not significant for the time being, and n equals 1, 2 and 3 for one-dimensional, two-dimensional and three-dimensional growth.

For

$$T(y) = \text{constant} \tag{2}$$

the relationship (1) becomes

$$\alpha_{ex} = (kt)^n \tag{3}$$

which corresponds to isothermal kinetics.
Another form of relationship (1) is

$$\alpha_{ex}^{1/n} = \int_0^t k[T(y)] \, dy \tag{4}$$

which is frequently used in the following.

The problem consists in establishing a relationship between α_{ex} and α with the general form

$$\alpha_{ex} = h(\alpha) \tag{5}$$

Introducing the notation

$$h^{1/n}(\alpha) = g(\alpha) \tag{6}$$

and taking into account relationship (4), we obtain

$$g(\alpha) = \int_0^t k[T(y)] \, dy \tag{7}$$

which is the formal integral kinetic equation for the processes of crystallization. Thus relationship (5) is important because it allows us, based on relationship (4), to derive eqn. (7), which contains the true degree of conversion.

From eqn. (7), taking the derivative with respect to time, the following relationships are obtained

$$g'(\alpha) \frac{d\alpha}{dt} = k[T(t)] \tag{8}$$

i.e.

$$\frac{d\alpha}{dt} = \frac{1}{g'(\alpha)} k[T(t)] \tag{9}$$

From eqn. (9), taking into account eqn. (6), we obtain

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = n\frac{h(\alpha)^{n-1/n}}{h'(\alpha)}k[T(t)] \tag{10}$$

where

$$n\frac{h(\alpha)^{(n-1)/n}}{h'(\alpha)} = f(\alpha) \tag{11}$$

is the formal conversion function.

Relationships (9) and (10) are the nonisothermal differential formal kinetic equations for the processes of crystallization.

Until now, the only relationship between α and α_{ex} is that due to Avrami [6] and has the simple form:

$$\alpha_{ex} = -\ln(1-\alpha) \tag{12}$$

or

$$\frac{\mathrm{d}\alpha}{\mathrm{d}\alpha_{ex}} = 1-\alpha \tag{13}$$

In previous work [8] using the formal kinetic theory of nucleation and growth of nuclei, we have shown that relationships (12) and (13) are not equivalent to relationships obtained from the above-mentioned theory.

Our purpose is to obtain other relationships of the form of eqn. (5) apart from Avrami's relationship.

DERIVATION OF NEW FORMAL RELATIONSHIPS BETWEEN α AND α_{ex} AS WELL AS THE CORRESPONDING KINETIC EQUATIONS

To find such relationships we shall start from the general relationship

$$\frac{\mathrm{d}\alpha}{\mathrm{d}\alpha_{ex}} = \phi(\alpha) \tag{14}$$

as the function $h(\alpha)$ can be obtained from it through a simple integration as follows

$$\int_0^{\alpha} \frac{\mathrm{d}\alpha}{\phi(\alpha)} = \int_0^{\alpha_{ex}} \mathrm{d}\alpha_{ex} \tag{15}$$

i.e.

$$\alpha_{ex} = \int_0^{\alpha} \frac{\mathrm{d}\alpha}{\phi(\alpha)} = h(\alpha) \tag{16}$$

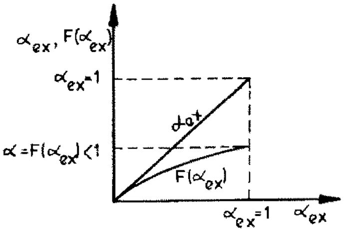

Fig. 1. Graphical illustration of relationship between α and α_{ex}.

Taking into account the meanings of α and α_{ex}, the following conditions should be valid:

(i) $t=0 \qquad \alpha_{ex} = \alpha = 0$ (17)

(ii) $t \neq 0 \qquad \alpha < \alpha_{ex}$ (18)

(iii) $\alpha_{ex} = 1 \qquad \alpha < 1$ (19)

(iv) The dependence $\alpha = F(\alpha_{ex})$ should appear as shown in Fig. 1.

(v) $$\frac{d\alpha}{d\alpha_{ex}} = \phi(\alpha) \qquad \phi(\alpha) > 0 \tag{20}$$

(vi) $$\frac{d^2\alpha}{d^2\alpha_{ex}} = \phi'(\alpha) \qquad \phi(\alpha) < 0 \tag{21}$$

In this paper only the following form of $\phi(\alpha)$

$$\phi(\alpha) = (1-\alpha)^r \qquad (r > 0) \tag{22}$$

is used suggested by eqn. (13) as a particular case for $r = 1$. Thus,

$$\frac{d\alpha}{d\alpha_{ex}} = (1-\alpha)^r \qquad (r > 0) \tag{23}$$

After variable separation and integrations one obtains from eqn. (23)

$$\int_0^{\alpha} \frac{d\alpha}{(1-\alpha)^r} = \int_0^{\alpha_{ex}} d\alpha_{ex} \tag{24}$$

and

$$\begin{cases} \dfrac{(1-\alpha)^{1-r} - 1}{r-1} = \alpha_{ex} \qquad (r \neq 1) & (25) \\ -\ln(1-\alpha) = \alpha_{ex} \qquad (r = 1) & (26) \end{cases}$$

As one can easily see, relationships (23), (25) and (26) as well as α_{ex} and α satisfy the conditions (i)–(vi) introduced above.

Using relationships (25) and (26) the following relationships corresponding to eqns. (7) and (10) can be written. Thus the following nonisothermal integral and differential equations are valid.

$$\left[\frac{(1-\alpha)^{1-r}-1}{r-1}\right]^{1/n}=\int_0^t k[T(y)]\,\mathrm{d}y \tag{27}$$

$$[-\ln(1-\alpha)]^{1/n}=\int_0^t k[T(y)]\,\mathrm{d}y \tag{28}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=nk[T(t)](1-\alpha)^r\left[\frac{(1-\alpha)^{1-r}-1}{r-1}\right]^{(n-1)/n} \tag{29}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=nk[T(t)](1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n} \tag{30}$$

From eqns. (27)–(30) the corresponding isothermal kinetic equations can be obtained by considering $T(t)$ as a constant, thus $k[T(t)]$ should be replaced simply by k.

For

$$T(t)=T_0+\beta t \tag{31}$$

eqns. (29) and (30) become, respectively

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A}{\beta}n(1-\alpha)^r\left[\frac{(1-\alpha)^{1-r}-1}{r-1}\right]^{(n-1)/n}\mathrm{e}^{-E/RT} \tag{32}$$

and

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A}{\beta}n(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n}\,\mathrm{e}^{-E/RT} \tag{33}$$

It should be emphasized that our considerations are valid for classical conditions [9] i.e. for $A=$ constant and $E=$ constant.

In isothermal conditions for the maximum crystallization rate at $\alpha_{\max,\mathrm{I}}$

$$\left.\frac{\mathrm{d}^2\alpha}{\mathrm{d}t^2}\right|_{\alpha_{\max,\mathrm{I}}}=0 \tag{34}$$

a condition which is equivalent to

$$\left.\frac{\mathrm{d}f(\alpha)}{\mathrm{d}\alpha}\right|_{\alpha_{\max,\mathrm{I}}}=0 \tag{35}$$

which leads after the detailed calculations to:

$$\alpha_{\max,\mathrm{I}}=\begin{cases}1-e^{(1-n)/n} & r=1\\ 1-\left(\dfrac{n+r-1}{nr}\right)^{1/(r-1)} & r\neq 1\end{cases} \tag{36}$$

As far as the nonisothermal case is concerned, we consider as representative the value $\alpha_{\max,\mathrm{NI}}$ for which

$$\left.\frac{\mathrm{d}^2\alpha}{\mathrm{d}T^2}\right|_{\alpha_{\max,\mathrm{NI}}}=0 \tag{37}$$

TABLE 1

The functions $g(\alpha)$ and $f(\alpha)$ and the values of $\alpha_{\max,\mathrm{NI}}$ and $\alpha_{\max,\mathrm{I}}$ for various values of r and n

No.	r	$g(\alpha)$	$f(\alpha)$	$\alpha_{\max,\mathrm{NI}}$	$\alpha_{\max,\mathrm{I}}$
1	1	$[-\ln(1-\alpha)]^{1/n}$	$(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n}$	0.632	0.000; $n=1$ 0.393; $n=2$ 0.487; $n=3$
2	2	$\left(\dfrac{\alpha}{1-\alpha}\right)^{1/n}$	$\alpha^{(n-1)/n}(1-\alpha)^{(n+1)/n}$	0.500	0.000; $n=1$ 0.250; $n=2$ 0.333; $n=3$
3	3	$\left[\dfrac{\alpha(1-\alpha/2)}{(1-\alpha)^2}\right]^{1/n}$	$\alpha^{(n-1)/n}(1-\alpha)^{(n+2)/n}(1-\frac{\alpha}{2})^{(n-1)/n}$	0.423	0.000; $n=1$ 0.184; $n=2$ 0.255; $n=3$
4	4	$\left\{\dfrac{\alpha\left[(\alpha^2/3)-\alpha+1\right]}{(1-\alpha)^3}\right\}^{1/n}$	$\alpha^{(n-1)/n}(1-\alpha)^{(n+3)/n}\left(\dfrac{\alpha^2}{3}-\alpha+1\right)^{(n-1)/n}$	0.370	0.000; $n=1$ 0.145; $n=2$ 0.206; $n=3$
5	0.5	$[2-2(1-\alpha)^{1/2}]^{1/n}$	$(1-\alpha)^{1/2}[2-2(1-\alpha)^{1/2}]^{(n-1)/n}$	0.750	0.000; $n=1$ 0.556; $n=2$ 0.640; $n=3$

Relationship (37) is satisfactorily approximated by [1]

$$g(\alpha)\frac{\mathrm{d}f(\alpha)}{\mathrm{d}\alpha}\bigg|_{\alpha_{\max,\mathrm{NI}}} + 1 = 0 \tag{38}$$

After performing the described calculations we obtain

$$\alpha_{\max,\mathrm{NI}} = \begin{cases} 1 - \dfrac{1}{e} & r = 1 \\ 1 - \left(\dfrac{1}{r}\right)^{1/r-1} & r \neq 1 \end{cases} \tag{39}$$

Table 1 contains the functions $g(\alpha)$ and $f(\alpha)$ as well as the values $\alpha_{\max,\mathrm{NI}}$ and $\alpha_{\max,\mathrm{I}}$ for various values of r and n. As can be seen from an inspection of the table, $\alpha_{\max,\mathrm{I}}$ depends on r and n, whereas $\alpha_{\max,\mathrm{NI}}$ depends only on r.

It is worthwhile to note that, by introducing relationship (39) into eqn. (25) or (26), we get

$$\alpha_{\mathrm{ex}} = 1 \tag{40}$$

a result which shows that, under isothermal conditions, when the degree of conversion reaches the value $\alpha_{\max,\mathrm{NI}}$ the idealized process is finished.

COMPARISON WITH EXPERIMENT

(1) In ref. 2 experimental data concerning $\alpha_{\max,\mathrm{NI}}$ for the crystallization of GeS_2 glasses from powders and bulk using heating rates in the range 10–50 K min^{-1} are given. For powders, $\alpha_{\max,\mathrm{NI}} \in [0.4020–0.4458]$ with an average value $\bar{\alpha}_{\max,\mathrm{NI}} = 0.428$. This result corresponds to a model for which $r = 3$. For bulk $\alpha_{\max,\mathrm{NI}} \in [0.4549–0.6071]$ with an average value $\bar{\alpha}_{\max,\mathrm{NI}} = 0.531$, which corresponds to a model with $r = 2$.

(2) In ref. 3 similar experimental data are given concerning the crystallization of $Ge_{40}S_{60}$ at heating rates in the range 5–20 K min^{-1}. For $\alpha_{\max,\mathrm{NI}} \in [0.465–0.523]$ with an average value $\bar{\alpha}_{\max,\mathrm{NI}} = 0.484$, thus corresponding to a model with $r = 2$.

(3) In ref. 10 experimental data concerning the kinetics of crystallization of nucleated polyethylene terephthalate are given. For $\beta \in [4–25]$ K min^{-1} and three samples the following results were obtained

Sample 1: $\bar{\alpha}_{\max,\mathrm{NI}} = 0.470$, which corresponds to $r = 2$

Sample 2: $\bar{\alpha}_{\max,\mathrm{NI}} = 0.365$, which corresponds to $r = 4$

Sample 3: $\bar{\alpha}_{\max,\mathrm{NI}} = 0.365$, which corresponds to $r = 4$

CONCLUSIONS

(1) From new relationships between α and α_{ex}, new kinetic equations describing the process of crystallization have been derived.

(2) A satisfactory agreement between the values of $\alpha_{max,NI}$ determined experimentally and the corresponding values calculated theoretically has been noted.

REFERENCES

1 T. Kemény and J. Šesták, Thermochim. Acta, 110 (1987) 113.
2 J. Málek and J. Klikorka, J. Therm. Anal., 32 (1987) 1883.
3 J. Málek, Thermochim. Acta, 129 (1988) 293.
4 J. Šesták, Thermophysical Properties of Solids, Academia, Prague, 1986, p. 190.
5 J. Šesták, V. Šatava and W.W. Wendlandt, Thermochim. Acta, 7 (1973) 403.
6 M. Avrami, J. Chem. Phys., 7 (1939) 1103; 8 (1940) 212; 9 (1941) 177.
7 P.W.M. Jacobs and F.C. Tompkins, in W.E. Garner (Ed.), The Chemistry of the Solid State, Butterworth, London, 1955, p. 207.
8 E. Urbanovici and E. Segal, Thermochim. Acta, 147 (1989) 231.
9 E. Urbanovici and E. Segal, Thermochim. Acta, 135 (1988) 193.
10 E. Schaff and H. Zimmermann, J. Therm. Anal., 33 (1988) 1053.