THE KINETIC EQUATION IN THE DTA STUDY OF THE SILICA GEL TO CRISTOBALITE TRANSFORMATION

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The importance of the choice of a suitable kinetic equation in the DTA study of the silica gel to cristobalite transformation is pointed out. It is shown that isothermal and non-isothermal data reported in the literature are better fitted by a Johnson—Mehl—Avrami equation with $n = 3$, rather than a "first-order" one.

The non-isothermal kinetics of the silica gel cristobalite transformation were studied by Das et al. [1]. A "first-order" reaction was assumed. The activation energy ($E = 453$ kcal/mole) derived from a single DTA curve by Piloyan's method [2] was not in agreement with that ($E = 150$ kcal/mole) obtained from several DTA curves, recorded at different heating rates, by Kissinger's method [3, 4].

The aim of this note is to show that the above discrepancy can be overcome if a suitable kinetic equation is assumed.

The complex process of nucleation and crystal growth required for the silica gel cristobalite transformation can be formally described by a Johnson–Mehl-Avrami (J.M.A.) [5] equation:

$$\frac{dy}{dt} = k^n t^{n-1}(1 - y) \tag{1}$$

where y is the extent of crystallization at time t, n is the reaction order and k is the overall rate constant, related to temperature T by an Arrhenius-type equation:

$$k = A \exp\left(-\frac{E}{RT}\right) \tag{2}$$

where the activation energy, E, is composed of the activation energies of the individual processes, nucleation, E_n, and crystal growth, E_g.

It should be noted that, for $n = 1$, Eq. 1 has the same form as the "first-order" equation $\frac{dy}{dt} = k(1 - y)$, assumed by Das to describe the silica gel cristobalite transformation.

If the silica gel cristobalite transformation is described by a J.M.A. equation, the Piloyan method (based on Borchardt's assumption that at any given temper-

ature the reaction rate $\dfrac{dy}{dt}$ is proportional to the temperature deflection ΔT as detected by DTA) leads, as recently proved [7], to the following equation:

$$\log \Delta T = \frac{E'}{4.57} \cdot \frac{1}{T} + \text{const.} \tag{3}$$

where $E' = nE$.

It is evident that $E' = E$ only if the silica gel cristobalite transformation is governed by a J.M.A. equation with $n = 1$ ("first-order" reaction) as supposed by Das. Otherwise, since with Eq. 3 it is not possible distinguish the activation energy E from the reaction order n, the latter can be calculated by comparing the E' value with that of E obtained by the following equation, which holds for several devitrification reactions [7−9]:

$$\log h = \frac{E}{4.57} \frac{1}{T_M} + \text{const.} \tag{4}$$

where h is the heating rate and T_M the peak temperature. As $\log T_M^2$ is practically a constant, the difference between the E values obtained by Eq. 4 and by Kissinger's equation:

$$\log \frac{h}{T_M^2} = \frac{E}{4.57} \cdot \frac{1}{T_M} + \text{const.} \tag{5}$$

is of a lower magnitude than the experimental error.

The values of E' (Eq. 2) and E (Eq. 5) obtained by Das and reported in Table 1 show that the silica gel cristobalite transformation is better described by a J.M.A. equation with $n = 3$ rather than by a "first-order" one.

Table 1

Kinetic parameters from isothermal and non-isothermal data

Methods	E, Kcal/mole	É, Kcal/mole	n
Isothermal	154 [10]		3
Kissinger	150 [1]		
Piloyan		453 [1]	
E'/E			3

The value $n = 3$ for the reaction order has been also confirmed by isothermal data. In Fig. 1 is shown an isothermal rate curve for the silica gel cristobalite transformation, derived from Verduch's data [10]. In view of its shape, it is evident that at the origin $t = 0$ the curve shows a null time derivative. For the condition $\left(\dfrac{dy}{dt}\right)_{t=0} = 0$ to obtain in Eq. 1, a reaction order $n \neq 1$ is required.

Moreover, by taking the logarithms of the integrated form of Eq. 1:

$$\log \log \frac{1}{1-y} = n \log t + n \log k - \log 2.3 \qquad (6)$$

and plotting $\log \log \dfrac{1}{1-y}$ vs. log t, from the slope of the resulting straight line (Fig. 2) a reaction order $n = 3$ has been calculated.

Finally, a J.M.A. equation with $n = 3$ describes [11] a process governed by instantaneous or previous formation of nuclei ready for a linear three-dimensional growth controlled by particle motion across the crystal-glass interface. This phase transformation model is consistent with the mechanism proposed [12] for cristobalite crystallization and with the activation energy value, which is the same as that for viscous flow in vitreous silica [13].
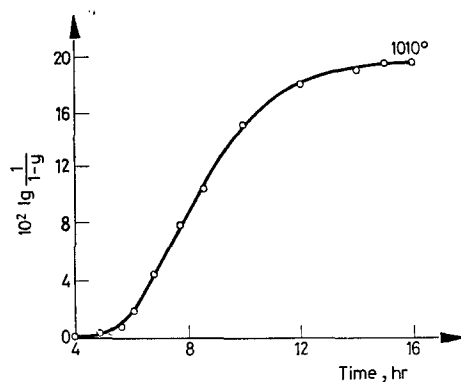

Fig. 1. Plot of $\log \dfrac{1}{1-y}$ vs. t $(T = 1010°)$ from Verduch's data [10]
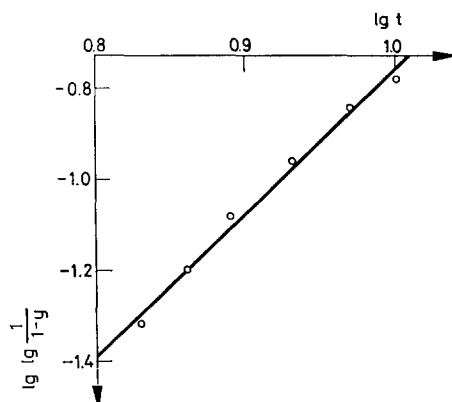

Fig. 2. Plot of $\log \log \dfrac{1}{1-y}$ vs. log t from data of Fig. 1

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RÉSUMÉ — On souligne l'importance du choix d'une équation cinétique convenable lors de l'étude par ATD de la transformation du gel de silice en cristobalite. On montre que les résultats cités dans la littérature obtenus en régimes isothermes et non-isothermes sont mieux interpolés par l'équation de Johnson—Mehl—Avrami avec $n = 3$ que par une équation du «premier ordre».

ZUSAMMENFASSUNG — Die Bedeutung der Wahl einer entsprechenden kinetischen Gleichung bei der DTA-Untersuchung von Kieselgel zur Cristobalittransformation wurde aufgezeigt. Es wurde bewiesen, daß isotherme und nichtisotherme Angaben der Literatur durch eine Johnson—Mehl—Avrami-Gleichung mit $n = 3$ besser interpoliert werden können als durch eine Gleichung »erster Ordnung«.

Резюме — Показана важность выбора приемлего кинетического уравнения при ДТА исследовании превращения силикагеля до кристобалита. Показано, что изотермические и неизотермические данные. приведенные в литературе, лучше интерполируются уравнением Джонсона—Мехла—Аврами с $n = 3$, а не «первым порядком».