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A MATHEMATICAL MODEL FOR THE KINETICS OF ISOTHERMAL RECRYSTALLIZATION IN SOLUTION*

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A self-consistent model has been constructed for isothermal recrystallization in solution that includes descriptions of three competing stages: dissolution of an initial metastable phase, nucleation of a stable phase in solution, and crystal growth. The kinetic equations have been solved by computer to examine the effects of the individual stage parameters on the kinetics. The calculations are compared with experimental data on zeolite synthesis, which shows that it is necessary to consider processes of nucleus multiplication in the solution.

INTRODUCTION

Research on the kinetics of the conversion of nonequilibrium states to equilibrium ones is as important in geochemistry as a knowledge of the equilibrium relations itself [1, 2]. Equilibrium concepts are involved in distinguishing metamorphic and mineral facies, in the physicochemical analysis of paragenesis, and in geothermometry and barometry. However, reliable use of geothermometers and barometers requires a knowledge of the response rate to changes in the external parameters, i.e., a definition of the characteristic relaxation times for nonequilibrium states. Only in that case can we have a reliable idea of the stage in the rock's geochemical history corresponding to the equilibria and why nonequilibrium relations are frozen in under certain circumstances, with metastable phases persisting for geological times.

In this connection it is necessary to examine the universal kinetic laws of mineral conversion, and to examine the contributions from the individual stages to the over-all rate, thereby defining the rate-limiting steps and providing an answer to the question of what information on the kinetic parameters can be provided not only by the degree of conversion but also by the grain size [2].

Here this problem is considered in general form for the case of isothermal recrystallization in solution, which is made up of the stages of initial phase dissolution, nucleation in the solution, and crystal growth for the new phase. The driving force of the transformation is the elevated chemical potential of the initial metastable phase. The transition from such a state to a stable one is related to random finite fluctuations of the nucleation type, and also to the transport of material needed for crystal growth. The solution provides a mechanism for nucleation and transport that acts at an appreciably higher speed than the analogous solid-phase reactions.

The process can serve as a model for various reactions occurring in natural systems, such as the conversion of pyroclastic material to a crystalline sediment under diagenetic conditions, recrystallization during metamorphism of rocks formed under other facies conditions [2] or of rocks under nonhydrostatic stress [3], and crystal growth from hydrothermal solutions when the wall

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rocks dissolve, etc. The model also has a direct bearing on the syntheses in geochemical experiments and mass crystallization in chemical engineering.

Kalinin [4] gives a list of papers on mineral formation kinetics, and in most of these attempts are made to describe the transformations by means of kinetic equations for the reactions [4, 5]. Although this approach is often successful, it cannot be taken as universal, since it is possible only when the reaction in one of the stages controls the over-all rate.

Nucleation and growth stages are incorporated into the Kolmogorov-Avrami model [6-10]. This model describes crystallization from a melt [6, 11] and solid-state transformations [11-13], but it cannot be used to simulate recrystallization via a solution because it does not incorporate the dissolution of the initial phase.

Attempts have also been made to use the crystal size distribution to obtain information on the relations between the kinetic parameters [10, 14-16]. The quantitative interpretation is based however only on solid-stage reactions. Also, arbitrary assumptions are made about the parameters, such as the constancy of the nucleation and growth rates [14] and that nucleation occurs in a single act. It has also been concluded [16] that such interpretations cannot be accepted on account of fluctuations in the face growth rates related to their defectiveness. However, the growth rates of crystals formed simultaneously can be characterized by an average quantity, while the over-all size distribution is determined by the evolution of this average characteristic.

Particular importance now attaches to self-consistent models describing competing mechanisms, models which enable us to simulate the natural processes. Mathematical experiments by computer provide a basis for detailed research on various stages, while parameter variation enables us to select the condition corresponding most precisely to experiment. A certain schematization of the actual process is balanced by the identification of decisive parameters and characteristics.

MODEL

Let us consider a water + component system corresponding in composition to the initial and newly formed phases. Isothermal recrystallization via a solution can be simulated as a simultaneous occurrence of three basic physicochemical processes: 1) metastable-phase dissolution, 2) stable-phase nucleation, and 3) crystal growth from the solution.

We will consider each stage in more detail. Let m_0 be the initial mass of the metastable phase, $m_1(t)$ the mass of metastable phase dissolved up to a given instant, and $m_2(t)$ the mass of crystals formed up to that instant, while m_{H_2O} is the mass of solvent.

The simplest dissolution law is that for a heterogeneous first-order reaction, which is described by

$$\frac{dc_1}{dt} = k_s S (c_0^* - c),\qquad(1)$$

where $c_1 = m_1(t)/m_{H_2O}$ is the mass of metastable phase dissolved up to a given instant as referred to the mass of liquid (solvent), $c = m_1(t) - m_2(t)/m_{H_2O}$ is the current concentration in the solution, c_0^* is the equilibrium metastable-phase concentration, and S is the variable surface area from which the dissolution occurs.

The coefficient k_s determines the rate of solution from a unit area at a supersaturation of one. Equation (1) corresponds to Nernst's equation [17] for the dissolution rate controlled by diffusion, where $k_s \sim D/\delta$, in which D is diffusion coefficient and δ is the width of the diffusion zone. If we denote by

$$c_2 = \frac{m_2(t)}{m_{H_2O}}$$

the concentration corresponding to hypothetical dissolution of all the crystals formed at a given instant, then $c = c_1 - c_2$. One of the basic interesting characteristics is the yield of the new phase or the degree of conversion $z(t)$, which is expressed in terms of c_2 by

$$z = \frac{c_2}{c_0^{**} - c_0},$$

where c_0 is the equilibrium concentration for the stable phase and $c_0^{**} = m_0 / m_{H_2O}$ is the mass of metastable phase referred to the mass of liquid.

If the metastable phase is represented by a porous structure, we can write an approximate expression for S, which will be used subsequently:

$$S = \alpha (c_0^{**} - c_1)^{\frac{2}{3}}. \tag{2}$$

Here α is an empirical shape coefficient.

By T_0 we denote some characteristic time, which thereby specifies the time scale. Let t' be the dimensionless time, which is related to the real time t by $t' = t/T_0$. Then the dimensionless parameters $\alpha T_0 k_s$, c_0^*, and c_0^{**} completely determine the dissolution. We assume that nuclei of the stable phase begin to be formed when concentration c_0 is reached, where $c_0 < c_0^* < c_0^{**}$. The dissolution is described by (1) before the nuclei begin to form, which in that case is integrated. In particular, if $\tilde{c}_0$ is the concentration at the initial instant ($\tilde{c}_0 < c_0$), then the time for the start of crystallization $t(c_0)$ is given by

$$t(c_0) = \frac{1}{\alpha k_s} \int\limits_{\tilde{c}_0}^{c_0} \frac{dc}{(c_0^{**} - c)^{2/3} (c_0^* - c)}.$$

For $t > t(c_0)$ it is necessary to solve the dissolution equations along with equations simulating the nucleation and crystal growth.

Let us restrict consideration to nucleation in the bulk of the solution and neglect heterogeneous nucleation. An empirical equation describing nucleation [18, 19] assumes a power-law dependence of the nucleation rate on the supersaturation:

$$\frac{dN}{dt} = k_N V_0 (c - c_0)^{M_N}, \tag{3}$$

where $N(t)$ is the number of nuclei formed up to time t, k_N is the nucleation rate per unit volume for a supersaturation of one, and V_0 is the liquid volume. The nucleation is usually divided into two stages: the induction period and that of active nucleation. In this model, the induction period can be distinguished nominally, and it is the more prominent the higher the power on the right in (3). Note that we have neglected surface effects by assuming that the nuclei are formed with zero radius.

The very simple equation (3) does not allow us to incorporate multiplication or secondary nucleus formation, which is related to the additional production of crystallization centers in the bulk in response to the existing crystals [20]. The rate of this process is evidently proportional to the surface area of the crystal that was already formed. Therefore, the necessary generalization can be attained by introducing into (3) a factor dependent on the total surface area of the crystals S_{cr}:

$$\frac{dN}{dt} = k_N V_0 (c - c_0)^{M_N} (1 + \varepsilon S_{cr}), \tag{4}$$

where ε is a coefficient defining the multiplication rate from a unit surface. The exponent M_N varies for different systems but on average approximates to $M_N = 4$ [18].

101

We have to describe the crystal growth in order to calculate S_{cr}, and we assume for definiteness that the crystals grow while retaining a cubic shape and do not interact directly one with another. The linear growth occurs independently on all faces and is described by

$$\frac{dL}{dt} = k_L (c - c_0)^{M_L},$$ (5)

where $L(t)$ is the size* of the crystal formed at time $t = 0$, while k_L is the linear growth rate for a supersaturation of unity. If the growth occurs in the diffusion region, $M_L = 1$. Also, $M_L > 1$ if the growth is controlled by reaction at the surface, but always $M_L < M_N$ [18, 19]. Let us introduce the characteristic size $L_0 = V_0^{1/3}$ and the dimensionless quantity $x = L/L_0$. Then the directionless parameter defining the growth will take the form

$$E = \frac{k_L T_0}{L_0}.$$ (6)

It is convenient to relate the time scale T_0 to the growth. For this it is sufficient to specify E, e.g., $E = 10^{-3}$. Then $T_0 = 10^{-3}(L_0/k_L)$ is the time necessary for a crystal to grow to a size $10^{-3}L_0$ at a supersaturation of one.

Using (3) and (5), we get an expression for c_2 based on the fact that $m_2(t)$ is the mass of the crystals at time t (crystallization began at $t = 0$, so $c(0) = c_0$). A crystal formed at time τ in time $t - \tau$ grows to a size $l(t, \tau)$ = $L(t) - L(\tau)$. In time $d\tau$ there are dN_τ nuclei formed, where

$$dN_\tau = k_N V_0 (c(\tau) - c_0)^{M_N} (1 + \varepsilon S_{cr}(\tau)) d\tau.$$ (7)

Consequently, at time t we have

$$m_2(t) = \rho_{cr} \int_0^t [L(t) - L(\tau)]^3 dN_\tau,$$ (8)

where ρ_{cr} is the crystal density. Also, S_{cr} is found similarly as

$$S_{cr} = 6 \int_0^t [L(t) - L(\tau)]^2 dN_\tau.$$ (9)

If we denote by $\rho_f = \beta \rho_{cr}$ the density of the liquid, we get an expression for $c_2(t)$:

$$c_2 = \frac{m_2}{\rho_f V_0} = \frac{1}{\beta} \int_0^t [x(t) - x(\tau)]^3 dN_\tau.$$ (10)

Equations (1, 2, 4, 5, 8-10) form a closed system of integrodifferential equations for the recrystallization dynamics. The initial conditions are

$$c_1(0) = c_0, \quad x(0) = 0,$$

i.e., the time is reckoned from the instant when the concentration c_0 is reached. This system enables us to simulate various states during the recrystallization. The basic dimensionless parameters are

$$G = \frac{\alpha k_s L_0}{k_L} E; \quad F = \frac{1}{\beta} \frac{k_N L_0^4}{k_L} E; \quad H = 6 \varepsilon L_0^2 \beta,$$ (11)

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*In this treatment, the linear growth rate is equal to twice the face advance rate.

and also the parameters that specify the depth of the metastability c_0^*/c_0, the relative concentration of the initial phase c_0^{**}/c_0, and the power-law dependence of the kinetic coefficients on the supersaturation M_N, M_L. Note that k_N and k_L in general are dependent on c_0, while k_s is dependent on c_0^*. If we refer the concentrations to c_0, it is convenient to use the parameters $k_L' = k_L c_0^{M_L}$, $k_s' = k_s c_0^{2/3}$, $k_N' = k_N c_0^{M_N}$ and the coefficients G', F', H', and E', which are expressed by means of (6) and (11). These parameters specify similarity criteria that enable us to simulate natural phenomena and engineering processes.

We reduce the basic system to a form convenient for numerical solution. We introduce new unknown functions:

$$A(t) = \int_0^t \frac{dN_\tau}{\beta F} ; \quad B(t) = \int_0^t \frac{dN_\tau}{\beta F} x(\tau);$$

$$D(t) = \int_0^t \frac{dN_\tau}{\beta F} x^2(\tau); \quad P(t) = \int_0^t \frac{dN_\tau}{\beta F} x^3(\tau).$$

The system takes the following form in the new variables:

$$\frac{dc_1}{dt'} = G(c_0^{**} - c_1)^{\tau/\imath}(c_0^* - c); \tag{12}$$

$$\frac{dx}{dt'} = E(c - c_0)^{M_L}; \tag{13}$$

$$\frac{dA}{dt'} = \lambda; \quad \frac{dB}{dt'} = \lambda x; \quad \frac{dD}{dt'} = \lambda x^2; \quad \frac{dP}{dt'} = \lambda x^3, \tag{14}-(17)$$

where

$$c = c_1 - F(Ax^3 - 3Bx^2 + 3xD - P),$$
$$\lambda = (c - c_0)^{M_N}[1 + H \cdot F(Ax^2 - 2xB + D)].$$

The system of six differential equations (12-17) with the initial conditions

$$c_1(0) = c_0; \; x(0) = 0; \; A(0) = 0; \; B(0) = 0; \; D(0) = 0; \; P(0) = 0$$

was solved numerically by the Runge-Kutta method in the fourth order with a BESM-6 computer. The following sections present the numerical results together with a discussion of the effects of the various parameters on the process.

The size distribution is one of the most important characteristics. We denote by $n(l)dl$ the number of crystals having sizes in the range from l to $l + dl$ at time T corresponding to the end of the process. As all the crystals are identical in linear growth rate, which is dependent only on the concentration of the crystallizing component in solution, we have

$$n(l)dl = dN = \frac{dN}{dt}(\tau)d\tau, \tag{18}$$

where dN is the number of crystals formed in time $d\tau$. The following obvious relation applies between τ and l:

$$l(\tau, T) = L(T) - L(\tau), \tag{19}$$

i.e., l is the linear size of a crystal formed at time τ. We use (19) to rewrite (18) in the form

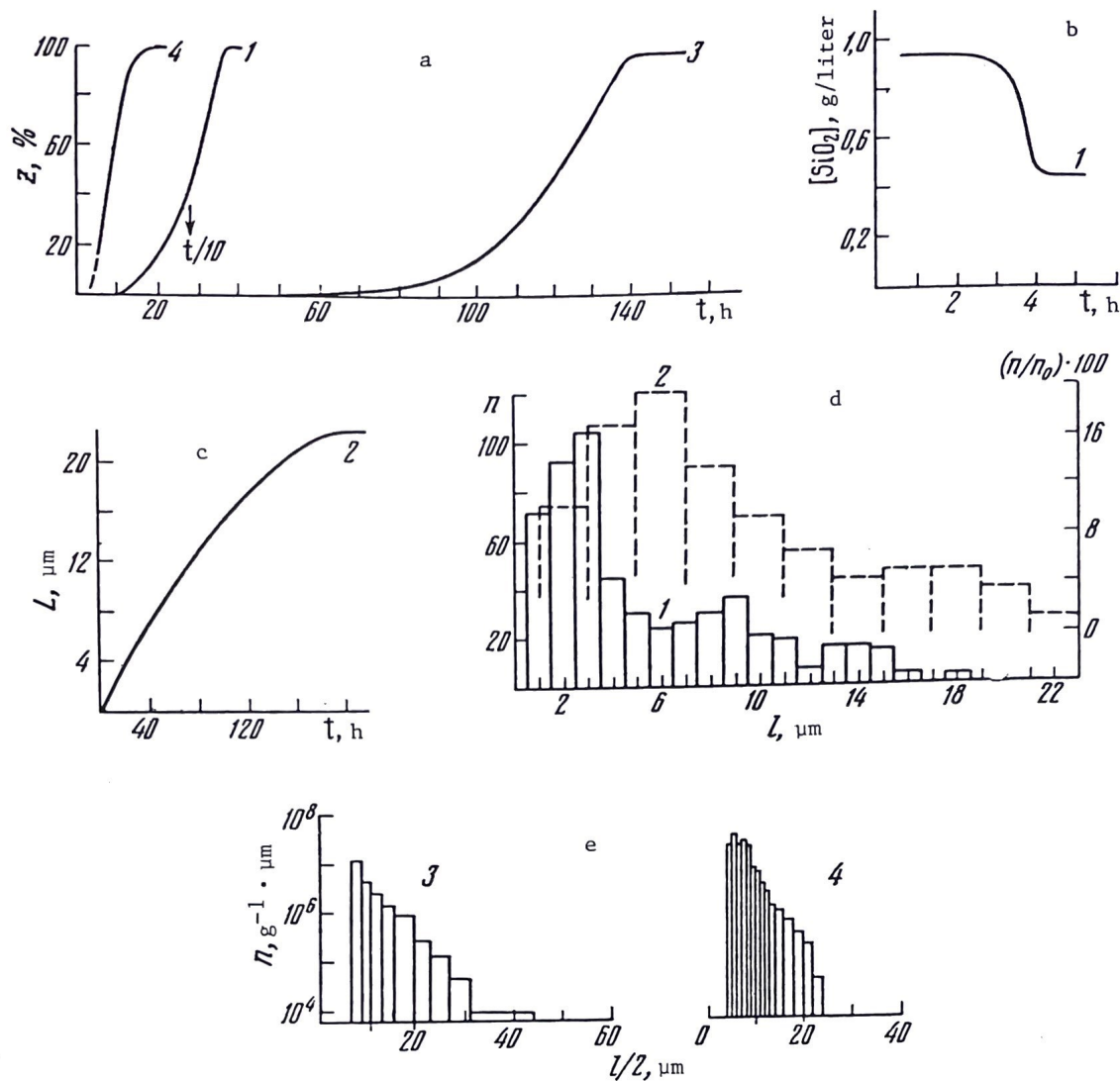$$n(l)dl = n(l)\frac{dl}{d\tau}d\tau = -n(l)\frac{dL}{d\tau}d\tau.$$

Fig. 1. Kinetic characteristics of zeolite crystallization: 1) NaA, 100°C, data of [21], 2) NaA, 90°C, data of [22], 3) Na mordenite, 150°C, without mixing, 4) Na mordenite, 150°C, with mixing, from data of [24, 25]; a) degree of conversion, b) silica concentration in solution, c) sizes of maximal crystals, d and e) size-distribution histograms, in which histogram e shows the number of particles in a fraction (on a logarithmic scale) as referred to 1 g of product and as divided by the radius interval in a fraction.

Then we have

$$n(l) = -\frac{dN(\tau)}{d\tau} \Big/ \frac{dL(\tau)}{d\tau}. \tag{20}$$

Then the solution enables us to calculate the values of $dN/d\tau$, $dL/d\tau$, $L(\tau)$, and $l(\tau, T)$ for each instant τ and then to use (20) to construct the size distribution.

EXPERIMENTAL TEST

Numerical implementation enabled us to examine the effects of various parameters. The model may be checked by means of the experimental data on zeolites, which are common minerals that are also produced artificially for use in adsorption techniques (molecular sieves) and in catalysis. Zeolites are synthesized from aluminosilicate mixtures (aluminosilicate gels, amorphous oxide mixtures, and glasses, which represent the metastable phase), and zeolites (the stable or relatively more stable phase) are produced by the action

of a solution at elevated temperatures. Figure 1 shows the kinetic character-
istics of the crystallization of the zeolites NaA and Na-mordenite. The ex-
perimental data [21-27] show that the yield of zeolite is described by an S-
shaped curve. The initial stage is characterized by vanishingly small yields,
and this is the induction period. The solution concentration and linear growth
rate remain practically constant throughout the transformation [21, 22], while
the size distribution has a peak indicating nonuniformity in the nucleation
rate as the process proceeds [21, 22, 25-27].

The Kolmogorov-Avrami [6-9, 27] formula or alternatively certain empiric-
al formulas [22, 24, 26] may be used to describe the zeolite recrystallization.
However, these are unable to describe all the experimental data, and they do
not correspond to the kinetic curves for a zeolite yield over the entire time
range. Also, this formal processing does not enable us to establish the roles
of the competing stages in the over-all effect. A detailed study may be based
on calculating various forms of the model by computer.

The following values were used for the dimensionless constants our of the
real relations for zeolite-forming systems:

$$\dot{c}_0/c_0 = 10, \quad \ddot{c}_0/c_0 = 100.$$

Also, the crystals grow in the kinetic range only at low supersaturations [18,
19]. Growth in the diffusion range is most probable for zeolites, as is evi-
dent from data on the constancy of the linear growth rate [22, 27]. Therefore,
the crystal growth and the dissolution were described by a first-order equa-
tion ($M_L = 1$ in (5)). Figures 2-5 show the results on zeolite synthesis and
characterize the behavior of the quantities that can be measured: the degree
of conversion z (graphs a), the concentration in the solution (graphs b), the
size of the maximal crystals (graphs c), and the size distributions (graphs d).
The time required to attain c_0 is usually negligible by comparison with the
over-all conversion time and is not shown. In the first stage in the calcula-
tions, the possibility of nucleus multiplication was ignored ($\varepsilon = 0$).
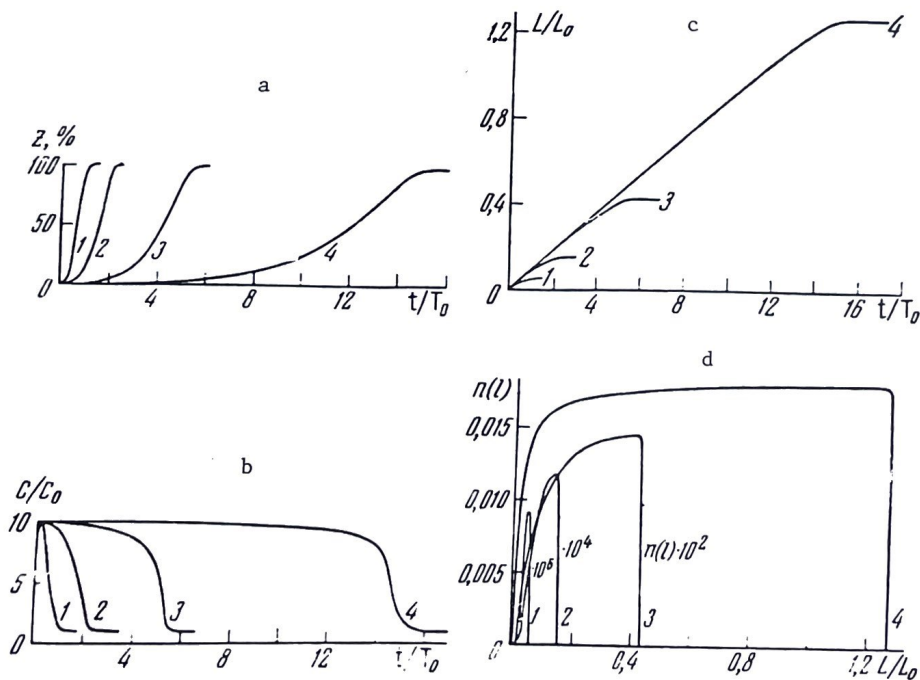

Fig. 2. Theoretical kinetic curves for recrystallization for various values of M_N in (4);
parameters $F' = 0.17$, $G' = 2.3$, $E' = 10^{-2}$, $H' = 0$ fixed: 1) $M_N = 8$, 2) $M_N = 6$, 3) $M_N = 4$, 4) $M_N = 2$.
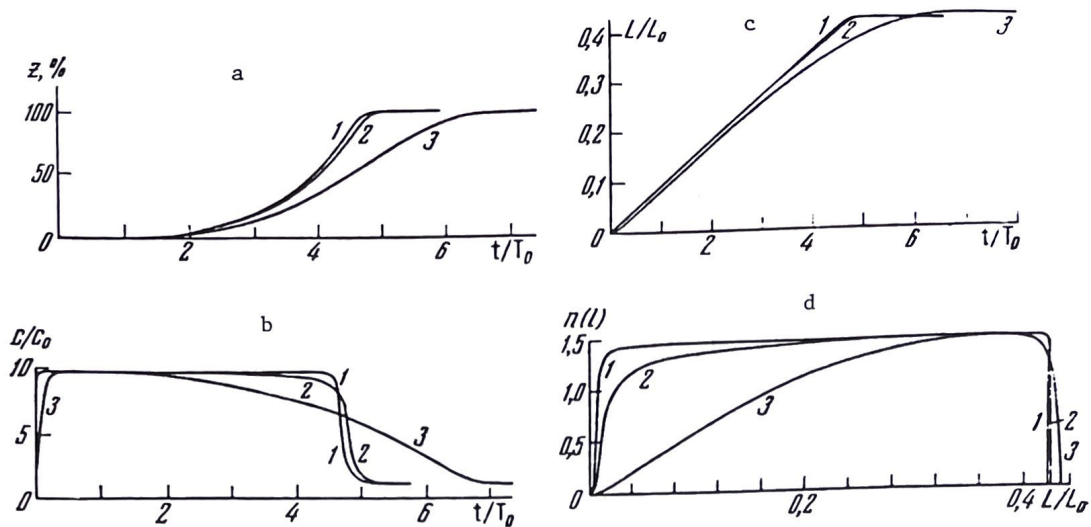
Fig. 3. Theoretical kinetic curves for recrystallization with various values for the dissolution rate G'; parameters $M_N = 4$, $F' = 0.17$, $E' = 10^{-2}$, $H' = 0$; fixed: 1) $G' = 1.2 \times 10^2$, 2) $G' = 1.2$, 3) $G' = 7.6 \times 10^{-1}$.

We do not know the exact value of M_N in (4), so calculations were performed for various values of this: 2, 4, 6, and 8 (Fig. 2). In general, there was no specific response of the kinetic curves to variation in M_N, which shows that it is necessary to examine the crystallization for various values of M_N. Let us therefore consider the effects of the rates of the individual stages for an average value $M_N = 4$, on the basis that the conversion time is shortened at higher values of M_N, as is the period of constant concentration, while the maximum crystal size is reduced and the size distribution becomes narrower (Fig. 2).

Figure 3 shows that a relative increase in the dissolution rate constant can provide the concentration constancy observed for zeolites [21, 22], which corresponds to the equilibrium solubility of the initial metastable phase, virtually throughout the conversion time. There is a certain critical value of the dissolution rate above which there is no marked effect on the process (Fig. 3).
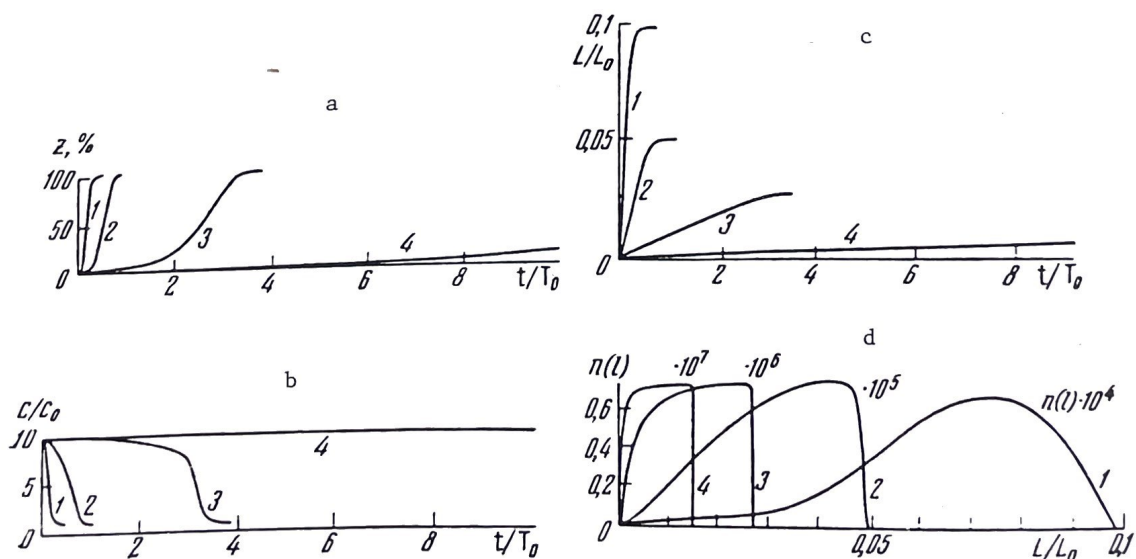

Fig. 4. Theoretical kinetic curves for recrystallization with various linear growth rates E'; parameters $M_N = 4$, $F' = 10^3$, $G' = 5$, $H' = 0$ fixed: 1) $E' = 0.1$, 2) $E' = 10^{-2}$, 3) $E' = 10^{-3}$, 4) $E' = 10^{-4}$.
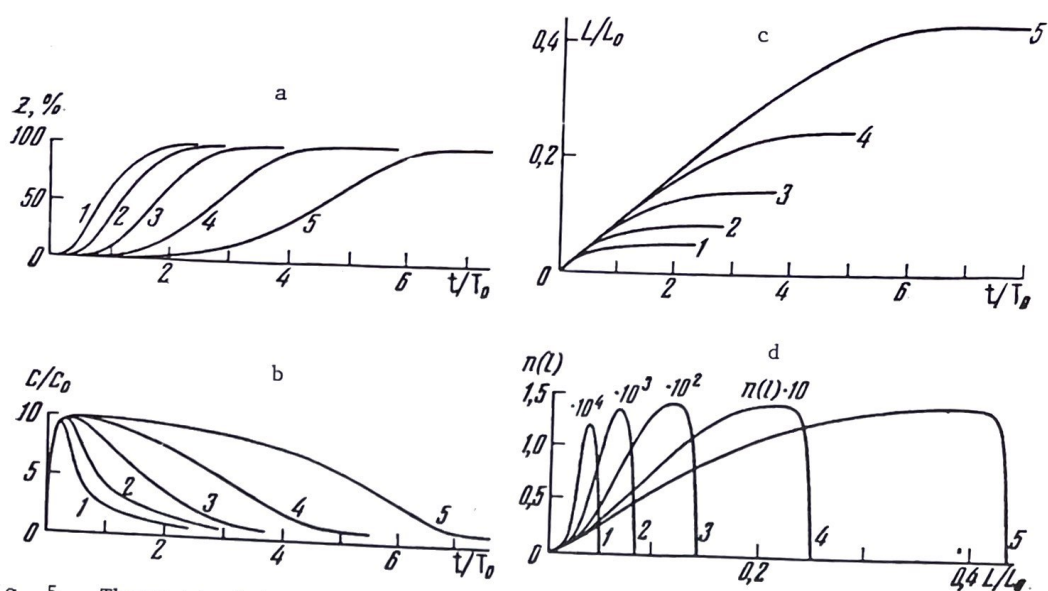
Fig. 5. Theoretical kinetic curves for recrystallization for various nucleation rates F'; parameters $M_N = 4$, $G' = 0.8$, $E' = 10^{-2}$, $H' = 0$ fixed: 1) $F' = 1.7 \times 10^3$, 2) $F' = 1.7 \times 10^2$, 3) $F' = 17$, 4) $F' = 1.7$, 5) $F' = 0.17$.

The over-all rate may be limited by the stages of crystal growth (Fig. 4) and nucleation (Fig. 5), where the growth has the more appreciable effect. Increase in growth rate and nucleation rate will accelerate the process, but with different effects on the size distribution. For example, the acceleration produced by mixing is accompanied by a reduction in crystal size [25], which indicates that the mixing affects primarily the nucleation rate.

All the yield curves in Figs. 2-5 are characterized by an initial part in which the mass of newly formed phase is vanishingly small. This part, which is observed experimentally, is the induction period.

The maximum crystal size in the range of constant concentration is linearly dependent on time. This is also in agreement with experiment. However, the size distributions have a flat part around the peak, whose width is dependent on the duration of the constant supersaturation in the solution.

There is no sharp peak, although this occurs for real size distributions in the product [21, 22, 25-27], which means that the nucleation rate in a real system follows a law more complicated than that described by (3). We therefore checked the effects of nucleus multiplication from (4) on the kinetic characteristics (Fig. 6). In that case, the calculated curves correspond to experiment also as regards the crystal sizes.

Therefore, the model describes all the features of zeolite crystallization known from the experiment. It confirms Zhdanov's [22] view that the process consists of three stages: dissolution of the amorphous phase, nucleation in the bulk of the solution, and crystal growth. An important point is that the dissolution rate must exceed a certain critical value, which provides the constant composition of the solution actually observed and a constancy of the linear growth rate occurring with diffusion control. Although the dissolution and the growth are limited by diffusion, the kinetic parameters may differ, since in a complicated real system the transport in these two stages may involve compounds differing in structure (silicate and aluminate ions, and aluminosilicate ones). On the other hand, the size distribution indicates essential nucleus multiplication in a real process, which is particularly pronounced on stirring [24, 25].

The major role of multiplication or secondary nucleation enables us to explain the effects of seeds in zeolite synthesis. It seems that the effect of a seed arises from its providing a surface for the crystalline phase to grow on and from its participation in secondary nucleation.
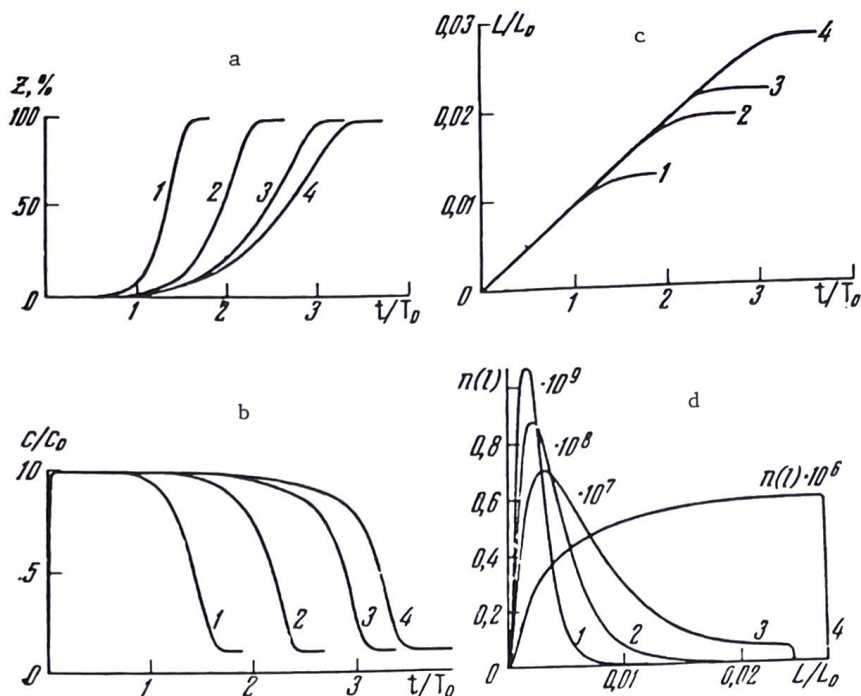
107

Fig. 6. Theoretical kinetic curves for recrystallization with various nucleus multiplication rates H'; parameters $M_N = 4$, $F' = 10^3$, $G' = 5$, $E' = 10^{-3}$ fixed: 1) $H' = 0.5$, 2) $H' = 5 \times 10^{-2}$, 3) $H' = 5 \times 10^{-3}$, 4) $H' = 0$.

The best of the empirical formulas for the zeolite yield is the Kolmogorov-Avrami formula [11]:

$$z = 1 - \exp(-kt^n)$$

with $n > 4$ [27]. The suitability of this expression can be checked for the curves derived from this model. It is sufficient to construct a graph for the yield of the new phase in $\ln \ln(1-z)^{-1}$, $\ln t'$ coordinates. The slope of the line corresponds to the value of n in the Kolmogorov-Avrami equation. Figure 7 shows the corresponding curves for cases with and without multiplication. The process evidently has two parts with different values of n. The factor $n > 4$ is a consequence of the nonuniformity in nucleation rate. Figure 7 shows that n increases towards the end of the process (the saturation falls more sharply and the nucleation rate varies more rapidly).

CONCLUSIONS

The model has a bearing on a very broad class of natural processes that include recrystallization through solution, as well as mass recrystallization in chemical engineering. It has proved possible to consider the interaction between the competing stages of dissolution, nucleation, and growth that make up the over-all process in the self-consistent model, which enables us to evaluate the effects of the kinetic parameters for the individual stages on the over-all recrystallization rate. The numerical approach enables us to formulate the assumptions clearly and to distinguish a set of dimensionless similarity criteria that define the process character.

The computer experiment has enabled us to examine various states in the recrystallization and to identify the role of each of the parameters. The data on the yield of the new phase and the size distribution in the crystals enable us to judge the relation between the rates of the individual stages, i.e., data obtained in actual physical experiments.

The model has been applied to the crystallization kinetics of zeolites, which represent an important technological process, and it has revealed a
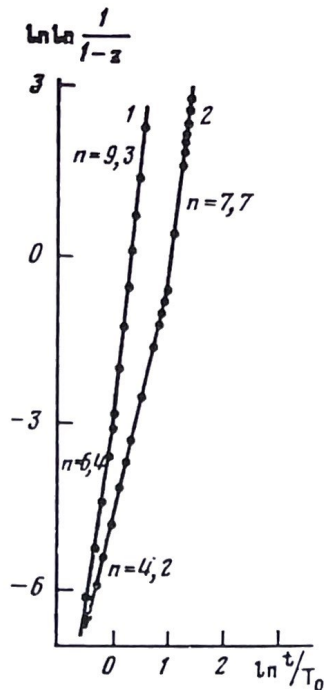
108

Fig. 7. Applicability of the Kolmogorov-Avrami interpolation formula in describing yield curves $M_N = 4$, $F' = 10^3$, $G' = 5$, $E' = 10^{-3}$; 1) $H' = 0$ (no multiplication), 2) $H' = 0.5$.

combination of parameters that reproduce the features of the reaction known from experiment: an induction period, a constancy in solution composition, constancy in crystal linear growth rate, and nonuniformity in the nucleation rate associated with multiplication.

This model appears to be the first of its kind, which justifies the simplifications in describing the individual stages. The latter however does not prevent us from obtaining good agreement with experiment. Improvements in the model may be related to the incorporation of more complicated laws for the dissolution, nucleation, and growth, including dissolution and growth controlled by chemical reactions as well as heterogeneous nucleation at the surfaces of the solid phases, as well as the involvement of nonisothermal processes.

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