Nucleation and Crystal Proliferation Kinetics:

Amorphous-Crystalline Transformation of Basic Copper Carbonates

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The transformation of amorphous basic copper carbonate precipitates into the crystalline form in aqueous solutions was experimentally studied. The unique blue-to-green color change and drastic volume reduction of the precipitates in transition made continuous observation and quantitative determination of the transformation process feasible. The transformation, which involves both nucleation and crystal growth proliferation, was autocatalytic. Experimental results are in good agreement with the rate equation formulated on the two-stage kinetics model postulated for the system. Also studied were the effects of temperature and precipitate concentration on the rate of transformation. In the temperature range between 34° and 39°C., the apparent nucleation activation energy was 19.8 kcal./g.-mole.

The art and science of crystallization are of interest to a wide range of physical and biological scientists and technologists (*1, 6, 11, 16, 20, 30*). The vast diversity of interest and objectives calls for the study of mechanism and techniques, such as to grow large perfect crystals, to grow crystals of uniform sizes, and to prevent the formation of crystals. The fundamental forces involved in all types of crystallization, whether in polymers, in organic and inorganic salts, or in metals, are believed to be essentially identical, but various crystallizing systems may show totally different behavior in the course of crystallization under different physical situations.

A great amount of work has been done on the various aspects of crystallization with crystallizing systems as diverse as insulin and synthetic zeolites. The effects of physical factors, such as degree of supersaturation, temperature, and cooling rate, on the growth rate of crystals (*7, 13, 18, 25*), size distribution (*4, 15, 17, 29*), and crystal morphology (*2, 26*) have been extensively investigated.

It is well established that there are two processes, nucleation and crystal growth, which are instrumental in the crystallization process. Because the elementary kinetic steps are little known and are specific for different systems, only empirical kinetic treatment of individual systems has been advanced by various workers (*10, 17, 21, 23, 24, 27*).

The system reported here is a complex inorganic precipitate, basic copper carbonate, formed in an aqueous medium. The stoichiometric relation of the reaction under controlled conditions conforms to the following equations (*9, 19*):

$$2Na_2CO_3 + 2CuSO_4 + H_2O = CuCO_3 \cdot Cu(OH)_2 + 2Na_2SO_4 + CO_2$$

$$CO_2 + H_2O + Na_2CO_3 = 2NaHCO_3$$

The initial precipitates formed by mixing aqueous sodium carbonate and cupric sulfate solutions were gelatinous and noncrystalline, but were able to transform themselves into crystalline particles of pure malachite on aging (*9, 28*).

The purpose of the present work is to study the kinetics of nucleation and crystal growth inherent in such transformation. Incidentally, this crystallizing system is particularly desirable in that the transformation process can be visually tracked.

THEORY

Crystal growth can be considered to consist of aggregation of increasing number of condensing molecules as indicated by the following series of arbitrary steps: Molecule—Cluster—Embryo—Nucleus—Crystal. The sequence (*31*) may be expressed symbolically:

$$\begin{aligned} \alpha + \alpha &= \alpha_2 \\ \alpha_2 + \alpha &= \alpha_3 \\ \cdot + \cdot &= \cdot \\ \cdot + \cdot &= \cdot \\ \alpha_{m-1} + \alpha &= \alpha_m \end{aligned}$$

The aggregation of molecules to become nuclei of critical size constitutes the nucleation process.

Nucleation can also originate with submicroscopic dust or other foreign particles P which contaminate the crystallizing system.

$$\begin{aligned} \alpha + P &= P\alpha \\ P\alpha + \alpha &= P\alpha_2 \\ \cdot + \cdot &= \cdot \\ \cdot + \cdot &= \cdot \\ P\alpha_{n-1} + \alpha &= P\alpha_n \end{aligned}$$

When an aggregate grows to become a particle exceeding the critical size as indicated by α_m or $P\alpha_n$, as the case may be, the free energy of the particle surmounts the growth energy barrier (*14, 22*). Further growth of the particle, or nucleus, is a much faster process and may follow dendritic or other branching patterns. The fast-growing branches readily break up by attrition into fragments which, in turn, become fresh nuclei to proliferate the growth-branching process.

In the case of basic copper carbonate, the rate of transformation of the initial noncrystalline precipitate into primary nuclei, that is, the rate of nucleation, is assumed to be proportional to the concentration and may be represented by the first-order rate equation.

$$\frac{d(ax)}{dt} = k_1 a(1-x) \tag{1}$$

or

$$r_1 = \left(\frac{dx}{dt}\right)_1 = k_1(1-x) \tag{2}$$

Once the first trace of crystals of critical size emerges, the rate of transformation is accelerated when successive generations of the secondary nuclei become available as a result of growth and fragmentation. By assuming first order with respect to the concentration of the noncrystalline precipitate and that of the crystalline malachite produced, respectively, the proliferation through growth and fragmentation is thus a second-order process. The differential rate equation for this process may be written as

$$\frac{d(ax)}{dt} = k_2 a(1-x)(ax) \tag{3}$$

or

$$r_2 = \left(\frac{dx}{dt}\right)_2 = k_2 ax(1-x) \tag{4}$$

In this stage, it may be noted that the primary process continues to operate as long as there is the noncrystalline magma. The overall rate of transformation of the noncrystalline precipitate during the proliferation period $(dx/dt)_T$ is therefore equal to the sum of the two individual rates r_1 and r_2.

$$\left(\frac{dx}{dt}\right)_T = k_1(1-x) + k_2 ax(1-x) \tag{5}$$

By rearranging Equation (5), we have

$$\int_0^x \frac{dx}{(k_1 + k_2 ax)(1-x)} = \int_\theta^t dt \tag{6}$$

Integration yields

$$t - \theta = \frac{1}{k_1 + k_2 a} \ln \frac{k_1 + k_2 ax}{(1-x)k_1} \tag{7}$$

Letting

$$\xi = k_2 a \tag{8}$$

and

$$\phi = k_1/k_2 a = k_1/\xi \tag{9}$$

Equation (7) becomes

$$t - \theta = \frac{1}{\xi(1+\phi)} \ln \frac{\phi + x}{(1-x)\phi} \tag{10}$$

Equations (5) and (10) are applicable to the period encompassing the incipience and completion of the proliferation stage.

Experimental determination of the degree of transformation is expected to enable one to evaluate ϕ and ξ, the nucleation and proliferation parameters of the crystallizing system.

EXPERIMENTAL METHOD

The method commonly used for studying the crystallization of solids is by x-ray diffraction. To facilitate the investigation of the noncrystalline to crystalline transition of a precipitate, samples of the precipitate for examination are frequently, by necessity, deactivated after designated time intervals by techniques such as lyophilization. Eanes and co-workers (*5, 6*) have recently reported such procedure in their study of the conversion of noncrystalline calcium phosphate to crystalline hydroxyapatite. However, quantitative measurements of solid crystallinity by x-ray diffraction are quite limited in precision, especially in the early stage of crystallization when the precipitate mass is predominately amorphous.

In the case of basic copper carbonate, in which dissolved and adsorbed carbon dioxide is expected to affect both the equilibrium and kinetics of the system in transition (*8, 19*), major difficulties would have to be overcome to develop a lyophilizing technique specific for this unstable system. Fortunately, as reported in previous work (*9, 28*), the transformation of basic copper carbonate is accompanied not only by a distinct color change from light blue to green, but also by a drastic reduction in its bulk volume. The transition therefore can be easily followed from the color change and from volume shrinkage of the precipitates accompanying the transformation. The ratio between the bulk volume of the initial amorphous precipitate and that of the final crystalline variety is about 10 or greater, depending on the concentration of the reacting solutions used. The large volume reduction has made it possible in this work to follow quantitatively the progress of the transformation process.

Preparation of the Amorphous Precipitates

The amorphous basic copper carbonate precipitates were prepared by adding slowly from a buret with agitation cupric sulfate solution to sodium carbonate solution in a beaker. Reagent grade sodium carbonate and cupric sulfate and carbon dioxide-free distilled water were used in making the respective reacting solutions. Prior to the determination of their concentrations, the reacting solutions were filtered to remove any foreign particles.

As an example, for one of the precipitation runs with a reactant molecular ratio $Na_2CO_3/CuSO_4$ of 1.10, 163.0 ml. of 0.85M cupric sulfate solution were added to 152.3 ml. of 1.00M sodium carbonate solution at 35°C., resulting in a light blue voluminous precipitate. The conditions, such as temperature and concentration of the reacting solutions, were varied in different runs, as will be seen later.

It may be mentioned here that there was a lowering of the temperature of the reacting solutions in the mixing by a fraction of 1°C., depending on the concentration of the solutions, thus indicating that the precipitation reaction is slightly endothermic.

Transformation of the Precipitates

The amorphous precipitate of basic copper carbonate in the form of uniform suspension was agitated for 5 min. and then poured into a 50-ml. Nessler color-comparing tube to the 50-ml. line. The tube was loosely stoppered. The Nessler tube had an I.D. of 16.8 mm. and a depth of 225 mm. to the 50-ml. marking, the total length of the tube being 298 mm. The Nessler tube with attached millimeter scale had been placed vertically in a constant-temperature water bath before the suspension was poured. A duplicate was made with a second tube.

The temperature of the water bath was maintained within ±0.02°C. and was set around 35°C. so that the transformation would be accomplished in no more than a few hours. The height of the precipitate was read and its color and appearance were noted after different time intervals. When no further noticeable changes were observed in both the height and appearance of the precipitate, the transformation was considered complete.

EXPERIMENTAL RESULTS AND DISCUSSION

The volume reduction accompanying the amorphous to crystalline transformation of basic copper carbonate in

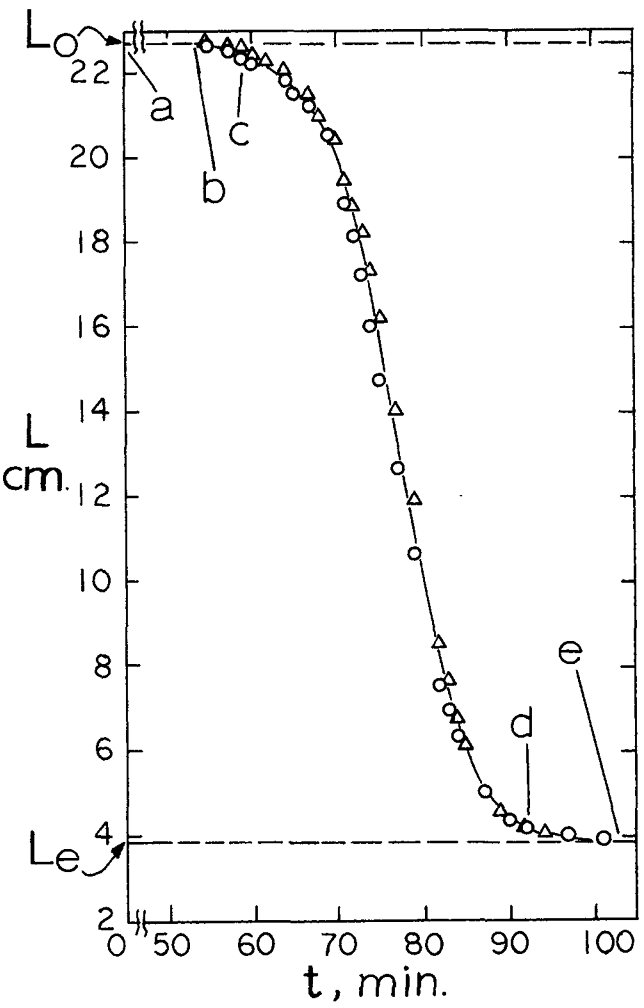

Fig. 1. Change of precipitate height with time. $Na_2CO_3/CuSO_4$ molecular ratio, 1.10; temperature, 37.22°C.; precipitate concentration as malachite, 0.220M; circles and triangles indicate data of duplicate tubes.

a typical run is shown in Figure 1. The conditions of the run were: temperature, 37.22°C.; reactant molecular ratio ($Na_2CO_3/CuSO_4$), 1.10; concentration of Na_2CO_3 solution, 1.00M; concentration of $CuSO_4$ solution, 0.85M. Four periods may be arbitrarily designated, as marked by points *a* to *e*, showing the metamorphosis of the precipitate in the course of the transformation.

The Induction Period (*a* to *b*). No change in the height and color of the voluminous blue precipitate was noted. This period was usually the longest in the transformation process.

The Incipience Period (*b* to *c*). In this period minute green crystals in the form of sporadic specks began to appear and the downward movement of the entire precipitate became discernible.

The Proliferation Period (*c* to *d*). In this period green crystalline particles appeared at a rapidly increasing rate amid the voluminous blue precipitate and at the expense of the latter. The rates of change in both height and color of the precipitate reached a maximum and then slackened.

The Tailing-Off Period (*d* to *e*). In this period the changes in height and in appearance of the precipitate became successively slower as the transition process approached completion.

It may be noted here that the induction period is assumed to be governed by Equation (2) and comprises the stage in which the primary nuclei are produced. Quantitative studies of the formative steps of the primary nuclei are beyond the scope of this report. Hence the volume changes observed represent the three periods subsequent to the emergence of the primary nuclei.

Based on the change of heights of the precipitate, the fractional volume reduction x is calculated from the relation

$$x = \frac{L_0 - L}{L_0 - L_e}$$

In the absence of direct experimental determination of the fractional crystallinity of the precipitate, it is reasonable to assume that the fractional volume reduction is proportional to the fractional crystallinity or fractional transformation; thus x represents both the fractional transformation and the volume reduction of the precipitate. The final dense particles were malachite as verified previously (*28*) by x-ray diffraction and chemical analysis.

Relative Rate of Nucleation and Crystal Proliferation

Figure 2 shows the variation of fractional transformation with time, calculated by using the data of Figure 1. The sigmoid-shaped $x - t$ curve, which is typical for an autocatalytic process, shows that before the embarkation of the proliferation stage, the nucleation stage took 53.8 min. after the termination of the precipitation operation. The proliferation stage lasted 47.7 min., as represented by the period between 53.8 and 101.5 min., when transformation of the precipitate approached completion.

With the fractional transformation x at different time t known, the parameters ξ and ϕ in Equation (10) may be evaluated by trial and error, which was done on an IBM 360 computer. On the basis of the experimental rate curve in Figure 2, the values for these two parameters are $\xi =$

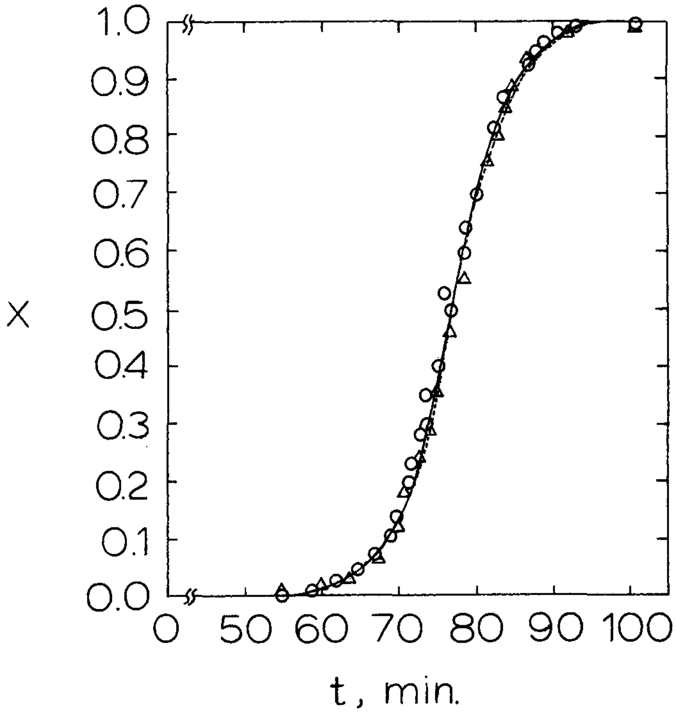

Fig. 2. Fractional volume change with time. $Na_2CO_3/CuSO_4$ molecular ratio, 1.10; temperature, 37.22°C.; precipitate concentration as malachite, 0.220M; dotted curve, calculated with $\xi = 0.250$ and $\phi = 0.00385$.

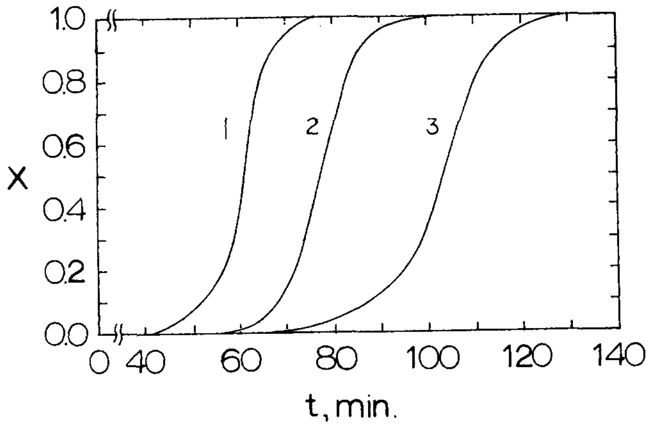

Fig. 3. Effect of temperature on rate of transformation. $Na_2CO_3/CuSO_4$ molecular ratio, 1.10; precipitate concentration as malachite, 0.220M; temperature: *curve 1*, 39.10°C.; *curve 2*, 37.22°C.; *curve 3*, 34.14°C.

0.250 and $\phi = 0.00385$. The good agreement between the experimental curve and that calculated with these parameters is shown in Figure 2. Referring to Equations (8) and (9), one can readily calculate the nucleation rate constant k_1:

$$k_1 = \xi\phi = 0.000963 \text{ min.}^{-1}$$

In respect to the proliferation rate constant k_2, it cannot be reliably evaluated based on Equation (8) before the growth reaction mechanism is clearly established and the concentration a identified. It is conceivable, however, that a is related in some manner to the concentration of the precipitate in the resulting solution, which was 0.440M in total copper or 0.220M as malachite, based on the amount of cupric sulfate solution used. In any event, the large ratio of ξ/ϕ signifies a large k_2/k_1 ratio, which, in turn, indicates that crystal proliferation is a much faster process than nucleation. The long induction period and the initial slow rise of the x versus t curve in Figure 2 delineate the relatively slow rate of nucleation. The paucity of nuclei in the early stage of the transformation process makes nucleation the rate-determining initial step, as was found in this work and those of others, such as the formation of Zeolite A (*12*) and of crystalline hydroxyapatite (*6*) from the respective noncrystalline initial precipitates.

The Effect of Temperature

The effect of temperature on the transformation rate was studied by measuring the height of precipitates in the Nessler tubes maintained at different temperatures. Specifically, for the same precipitate preparation with the reactant molecular ratio at 1.10 as described earlier, three constant-temperature baths were used, each of which held two tubes.

Presented in Figure 3 are the x versus t curves for a typical run with the temperatures of the three baths maintained at 34.14°, 37.22°, and 39.10°C., respectively. As expected, the higher the temperature the shorter was the induction period. Based on the length of the induction time θ and assuming that the nucleation process is rate-determining, the apparent nucleation activation energy E_a may be calculated by the relation

$$\frac{d\ln(1/\theta)}{d(1/T)} = \frac{E_a}{R}$$

In Figure 4 is the Arrhenius plot, having the logarithmic reciprocal induction time and reciprocal absolute temperature, respectively, as the ordinate and abscissa. The slope of the straight line in the semilogarithmic plot yields an apparent nucleation activation energy of 19.8 kcal./g.-mole. This activation energy represents essentially the energy barrier to be overcome in the nucleation of the amorphous precipitate to form crystals of critical size (*14*, *31*) prior to the onset of the proliferation stage.

The Effect of Concentration

The amorphous precipitate suspensions used here were of different concentrations and were prepared by adding a cupric sulfate solution to sodium carbonate solutions of different concentrations, the reactant molecular ratio being again fixed at 1.10. The concentration of the limiting reactant, that is, the total copper concentration, in the resulting suspensions ranged from 0.198 to 0.486M, or 0.099 to 0.243M, as malachite $CuCO_3 \cdot Cu(OH)_2$. The fractional transformation versus time curves for the different concentrations are shown in Figure 5.

The lower ends of the four curves in Figure 5 represent the respective induction periods for nucleation, which become longer with decreasing concentration of the initial noncrystalline precipitates. Within the concentration range represented by curves 1 to 3, the effect of the initial magma concentration on the subsequent crystal proliferation is not appreciable. The effect, however, becomes noticeable as shown by the exceptional shape of curve 4, for which the initial magma concentration was 0.099M as

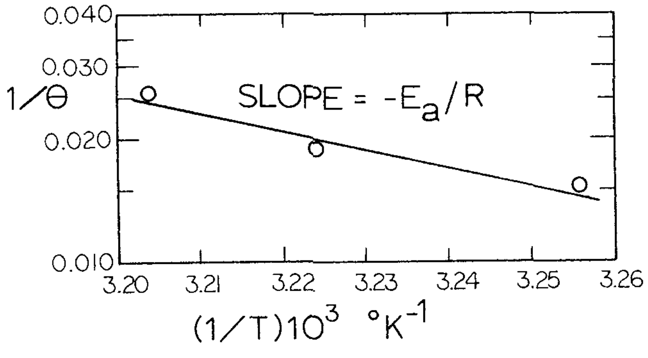

Fig. 4. Logarithmic reciprocal induction time versus reciprocal absolute temperature. $Na_2CO_3/CuSO_4$ molecular ratio, 1.10; precipitate concentration as malachite, 0.220M.

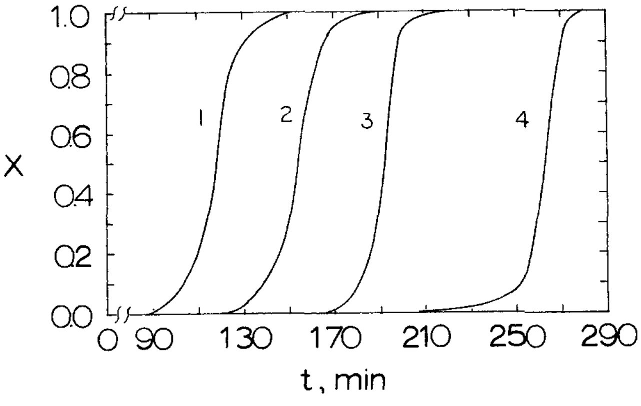

Fig. 5. Effect of precipitate concentration on rate of transformation. $Na_2CO_3/CuSO_4$ molecular ratio, 1.10; temperature, 35.02°C.; precipitate concentration as malachite: *curve 1*, 0.243M; *curve 2*, 0.183M; *curve 3*, 0.141M; *curve 4*, 0.099M.

malachite. As reported in the literature (*3, 24, 25, 27, 30*), the order of reaction of crystallizing systems and of autocatalytic chemical reactions of solids varies in a considerable range, from lower than first order to fourth order, dependent mainly on the concentration of the active species undergoing transformation. Further work is needed to establish the effect of concentration on the kinetics of phase transformation of this system.

In the formation of crystalline hydroxyapatite from calcium chloride and ammonium hydrogen phosphate solutions, Eanes and co-workers (*6*) proposed that the initial noncrystalline precipitate serves as a reservoir to supply the ions with which the final crystals are constructed. In view of the complexity of the reactions accompanying the initial precipitation and the subsequent conversion of this system, no attempts are made here to postulate the intricate mechanism and kinetic steps involved.

SUMMARY AND COMMENTS

The unique characteristics of basic copper carbonates, that is, volume and color changes in the course of crystallization, made kinetic study of the transformation process possible. The conversion of the initial blue amorphous precipitate into the green crystalline variety is attributed to two arbitrary, but distinctive stages: the nucleation stage and the crystal proliferation stage. The compatibility of the experimental rate of transformation with the rate equations derived from the two-stage model serves to substantiate that the proliferation of crystals is autocatalytic, and the proliferation stage is preceded by the longer nucleation or induction stage. The results thus shed light on the familiar but little understood domain of autocatalysis in phase transformation which exists in a multitude of physical and biological systems and situations.

During the proliferation stage, both nucleation and crystal growth-fragmentation are operative, although the latter process is far faster throughout this period. For a sparingly soluble precipitate such as this system, after the nuclei attain a certain critical size further growth results not in the formation of large crystals, but in the proliferation of small crystals of relatively uniform size. The crystals obtained in this work measure between 2.6 and 12 μ; most of them are in the 6 ± 2 μ range.

Extension of the model and rate equations to the interpretation of phase transformation kinetics of other crystallizing systems has been undertaken, and is to be discussed in a separate report.

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NOTATION

a = initial precipitate concentration
E_a = nucleation activation energy
k_1 = nucleation rate constant
k_2 = crystal proliferation rate constant
L = height of precipitate at any time t
L_e = final precipitate height
L_0 = initial precipitate height
r_1 = nucleation rate
r_2 = crystal proliferation rate
R = universal constant
t = time
T = absolute temperature
x = fractional transformation of initial precipitate

Greek Letters

α = aggregating molecule or species
θ = induction time for nucleation
ξ = k_2a, or crystal proliferation parameter
ϕ = k_1/k_2a, or nucleation parameter

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