Calculation of Kinetic Parameters for Crystallization Processes

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Abstract: In this work, kinetic data of crystallization processes have been determined by measurement of the intensities of reflection of X-ray diffraction spectra and modeled using the Avrami-Eroféev and Jander expressions. We have created a simple Microsoft Excel spreadsheet that allows students to calculate the kinetic data. Students will be able to calculate the kinetic parameters of any crystallization process, for example, hydrothermal crystallization of catalytic materials like zeolites. The possibility of using the spreadsheet with different models or expressions and discriminating among them is also validated by comparing the model results with experimental data (differential thermal analyses, DTA) from papers available in the recent literature.

Introduction

Crystallization is one of the basic processes in the final treatment of products in the chemical industry. Although industrial crystallization has been used in practice for centuries, the earliest theoretical works in this field that have any practical importance appeared as late as the end of the 19th century. Kinetic data on the crystallization process are of basic importance for the design of industrial crystallization equipment. There are a number of theories on the crystallization process, but the discrepancy between the theories and experiment is often remarkable because of the over-simplification of model concepts.

Two of the most important examples of a crystallization process are the hydrothermal crystallization of zeolites and solid-state crystallization (solid–solid crystallization). In this work, the application of two kinetic models in the crystallization of layered sodium silicate, particularly δ-$Na_2Si_2O_5$, is shown. This silicate has significant importance in the detergent industry because it is a new detergent builder (it chelates the ions that contribute to water hardness) in nonphosphate detergent formulations.

Theory

When an amorphous solid sample is heated, one of the possible changes it undergoes is crystallization. Information on the kinetics and mechanism of solid crystallization is of both practical and theoretical importance. Numerous observations confirm that the crystallization of solid reactants is generally initiated at defective regions of the amorphous solid, such as the surface or, more specifically, the points of emergence of dislocation at the surface. Nuclei of crystallization are thus formed, and the resulting disruption causes strain in the neighboring regions of unreacted amorphous solid resulting in growth of the nuclei (Figure 1). The investigation of the kinetics of crystallization processes has long constituted an important area of study within the field of solid-state chemistry.

In the treatment of the solid state, the kinetic model accounts for rate characteristics through interface advance involving, perhaps, nucleation and growth and/or diffusion processes. Two of the most widely used kinetic models are the schemes proposed by Avrami and Eroféev and the Jander expression. The Avrami–Eroféev relationship assumes that a solid-state transformation proceeds by a nucleation and growth mechanism and takes into account the coalescence and ingestion of other nuclei as the new phase grows, whereas the Jander equation indicates a diffusion-controlled reaction.

The Avrami–Eroféev Expression. The study of crystallization kinetics in solids involves measurement of the extent of reaction, α, as a function of time, t.

Crystallization curves such as those shown in Figure 2 are often simulated using the Avrami–Eroféev expression [1]. This kinetic expression has been widely used in solid-state chemistry as a mean of modeling, for example, phase transitions and crystal growth, and it is often used to interpret the crystallization curves of silicates as zeolites [2–4]. The Avrami–Eroféev expression simply relates the extent of reaction, α (the fraction of crystalline product), to the time coordinate, t, and may be expressed as:

$$\alpha = 1 - \exp\{-[K(t - t_0)]^n\} \tag{1}$$

where K is the rate constant, and n, the Avrami exponent. The value of n contains information about the mechanism of the process studied and the growth geometry, and it is similar to the reaction order. A value of n close to 1 denotes surface crystallization, one-dimensional growth, while a value of 3 implies bulk crystallization or three-dimensional growth. According to Hulbert, Avrami exponents close to 0.5 are expected when a reaction is diffusion controlled [5]. The instructor should discuss with the students the meaning of the different values of the Avrami exponent. The value of t_0 is the induction time of the process studied, a period which describes the time at which the X-ray diffraction (XRD) reflections start to appear. In our case, the crystallization of δ-$Na_2Si_2O_5$

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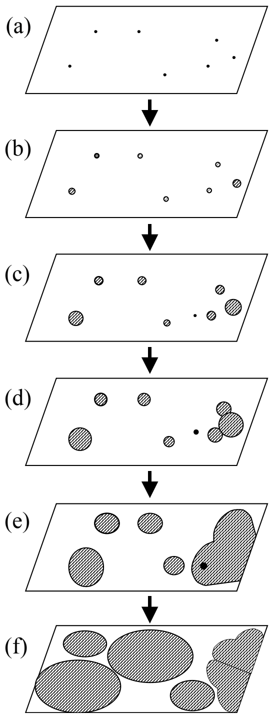

Figure 1. Formation and growth of nuclei of product in the crystallization of solids: (a) nucleation sites, (b) first nuclei formed, (c) growth and further nucleation, (d) overlap of nuclei, (e) ingestion of a nucleation site, (f) continued crystallization growth.

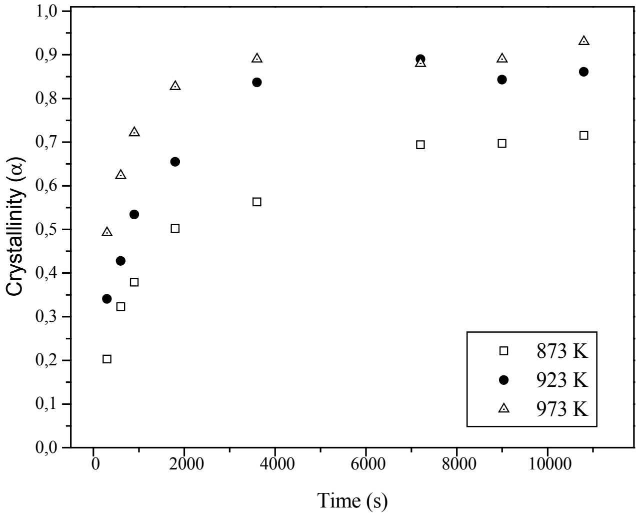

Figure 2. Kinetics of crystallization of δ-$Na_2Si_2O_5$ at different temperatures.

required the use of crystal seed, so that t_0 is equal to zero. Then eq 1 can be written in the form

$$\alpha = 1 - \exp\left[-(Kt)^n\right] \tag{2}$$

The Jander Approximation. This model is used for diffusion-controlled solid-state reaction kinetics. Jander [6] established that for crystallization processes where crystal growth occurs from nucleation sites, the largest part of the crystallization may be expressed as

$$[1 - (1 - \alpha)^{1/n}]^2 = \kappa(t - t_0) \tag{3}$$

The rate constant is designated κ to differentiate it from the Avrami–Eroféev rate constant used above. In our case t_0 is also equal to zero, and n has a similar meaning to the Avrami exponent. In the case of the Jander equation, n must be equal to three, to indicate that a three-dimensional diffusion is controlling mechanism of crystallization.

From eq 3, the fraction of crystalline product, α, can be expressed as:

$$\alpha = 1 - [1 - (\kappa t)^{1/2}]^n \tag{4}$$

The Relationship Between the Rate Constant and the Temperature. The rate of a reaction depends on the temperature, thorough variation of the rate coefficient (K, or κ in our case). According to Arrhenius,

$$\mathrm{Ln}\, K = -E_a/(RT) + \mathrm{Ln}\, A_0 \tag{5}$$

Where T is the temperature in Kelvin, R is the gas constant in kJ mol^{-1} K^{-1}, E_a is the activation energy in kJ mol^{-1}, and A_0 is a constant called the frequency or pre-exponential factor.

Consequently, when Ln K or Ln κ is plotted versus $1/T$ we can get the kinetic parameters E_a and A_0 from the slope and intercept, respectively.

XRD Characterization. The means of characterization used in this work is the XRD technique. X-ray powder diffraction was developed as early as 1916 for the characterization of materials. The diffraction pattern is the fingerprint of any crystalline phase, and powder diffraction is used extensively to identify the mixture of phases and the crystallinity of any solid. The availability of diffractometers interfaced to low-cost personal computers and the development of commercial software for data analysis, user friendly and graphical, have contributed to make powder diffraction a routine technique in laboratories of any university.

Powder diffraction is able not only to identify but also to quantify the crystalline fraction of the materials such as zeolite or zeolite-like materials. There are many books on X-ray diffraction. Detailed treatments of the diffraction by crystals and powders can be found in the book by Azaroff and Burger [7]. Descriptions of the experimental methods are given in the less theoretical books by Klug and Alexander [8] and Schwartz and Cohen [9]. A description of the methods currently in use for powder diffraction can be found in the "Course Notes" edited by the Mineralogical Society of America [10].

This work shows an easy method to calculate the fraction of crystalline product, α. This fraction may be defined as the ratio of the peak intensity at time t, I_t, to the maximum peak intensity when crystallization is complete, I_{max}. In our case, the standard δ-$Na_2Si_2O_5$ used as seed must be considered 100 % crystalline so that its peak intensity is I_{max}. The calculated value of I_{max} is later used to normalize data and to present kinetic curves in terms of α according to the following:

$$\alpha = I_t/I_{max} \tag{6}$$

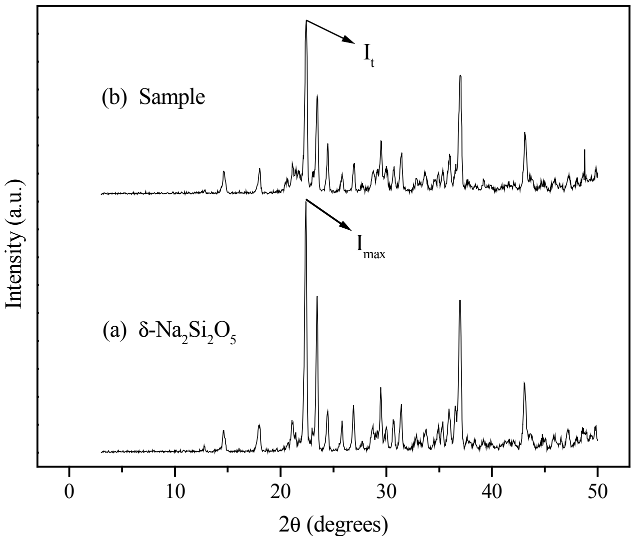

Figure 3. X-ray powder pattern of the standard δ-$Na_2Si_2O_5$ and a sample with a high crystallinity.

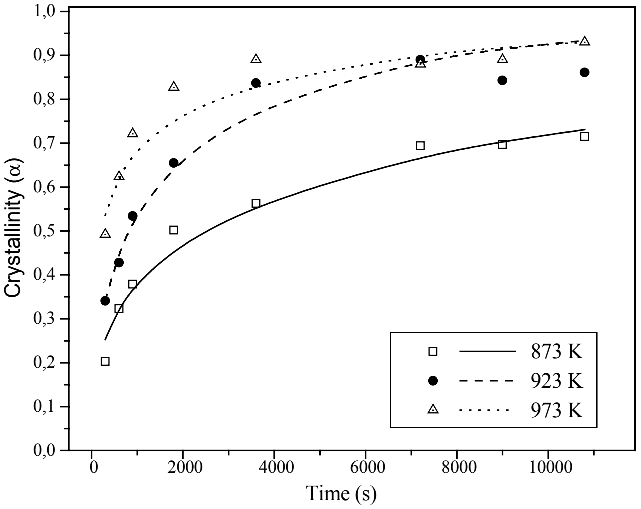

Figure 4. Crystallization kinetics. Experimental data and best fit of Avrami–Eroféev model at different temperatures.

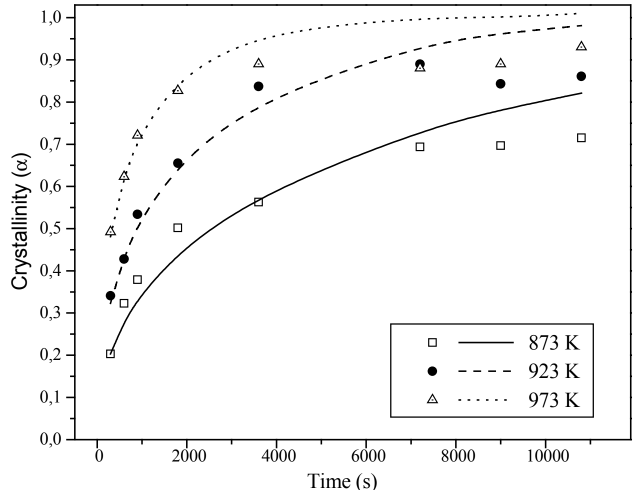

Figure 5. Crystallization kinetics. Experimental data and best fit of Jander model at different temperatures.

The X-Ray powder pattern of the standard δ-$Na_2Si_2O_5$ used as seed (100 % of crystallinity) and a sample with high crystallinity (about 75 %) are shown in Figure 3. There are other methods for the determination of the crystalline fraction (for example, the sum of the areas of two peaks has been used to calculated the crystallinity of birnessite [11]), and, therefore, the numerical values of crystallinity obtained by different laboratories cannot be directly compared. Despite this limitation, the information, regarded on relative basis, is essential for the studies on synthesis and modification of crystalline materials.

All the XRD patterns were carefully recorded under identical conditions for crystallinity determination such that the peak intensities correctly reflect the corresponding crystallinity of the sample, and they were obtained for three or four times in order to check the reproducibility of the data. The reproducibility of the XRD data was high; the errors were lower than 7 wt %.

Experimental

Before the experiment begins, the instructor must explain the theoretical concepts of each of the models to be used and the theoretical basis of X-ray Powder Diffraction.

Example: δ-$Na_2Si_2O_5$ Crystallization. Crystallization experiments can be carried out in an air atmosphere using a temperature-controlled furnace. The amorphous sodium silicate and the seed must have the same molar ratio $SiO_2/Na_2O = 2$ and a particle size < 0.1 mm. Both are available from IQE (Industrias Químicas del Ebro S.A. FAX: +34 976 57 25 57; e-mail: iqe@iqe.es) or from Clariant Gmbh (FAX: +49 61967578526; e-mail: Lutz.Schaefer@clariant.com). A 20 wt % of seed is required, so that t_0 is equal to zero. The amorphous silicate and the seed are first mixed. Then, the mixture (10 g) is placed in a 100-mL porcelain cup and introduced at the selected temperature and reaction time. Different porcelain cups must be used for different reaction times. Crystalline products obtained must be milled to a particle size lower than 0.5 mm before their XRD characterization.

Results and Discussion

The fit of the experimental data obtained by the students to the models pointed out in the "Theory" section can be performed using Microsoft Excel 7.0 spreadsheets (provided in the supporting material). Note that the fits of the two models to the α versus time data involves a nonlinear least-squares fit in which both K and n are floated. The relative error of each data point must be calculated as follow:

$$E(\%) = \left|\frac{\alpha\ (\exp) - \alpha(\mathrm{th})}{\alpha\ (\exp)}\right| \times 100 \qquad (7)$$

where α(exp) are the experimental data for α and α(th) are the theoretical data for α obtained by the models shown by eqs 2 and 4. Finally, the mean error of each kinetic parameter is calculated and should be lower than 10 %. Once good fits of the models to the experimental data have been observed (mean error < 10 %), the rate constants for all temperatures are calculated. Then, by using the Arrhenius expression, the activation energy and the frequency factor of the crystallization process can be calculated. Finally, the standard deviations for both the ln A_0 and E_a/R values are calculated in the spreadsheet (see the supporting material). The statistical

Table 1. Rate Constant, *n*, and Kinetic Parameters Obtained in the crystallization of δ-$Na_2Si_2O_5$ by the Avrami–Eroféev and Jander Expressions

	Avrami–Eroféev expression			Jander expression		
T (K)	K (s^{-n})	n	Kinetic parameters	κ(s^{-n})	n	Kinetic parameters
873.15	$1.77{\cdot}10^{-4}$	0.41	$E_a = 153.5$ kJ mol^{-1}	$1.76{\cdot}10^{-5}$	3.0	E_a= 140.3 kJ/mol
923.15	$6.26{\cdot}10^{-4}$	0.52	$A_0 = 2.8{\cdot}10^5\ s^{-n}$	$4.95{\cdot}10^{-5}$	3.0	$A_0 = 4.3{\cdot}10^4\ s^{-n}$
973.15	$1.55{\cdot}10^{-3}$	0.35	$R = 0.998$	$1.28{\cdot}10^{-4}$	3.0	$R = 0.999$

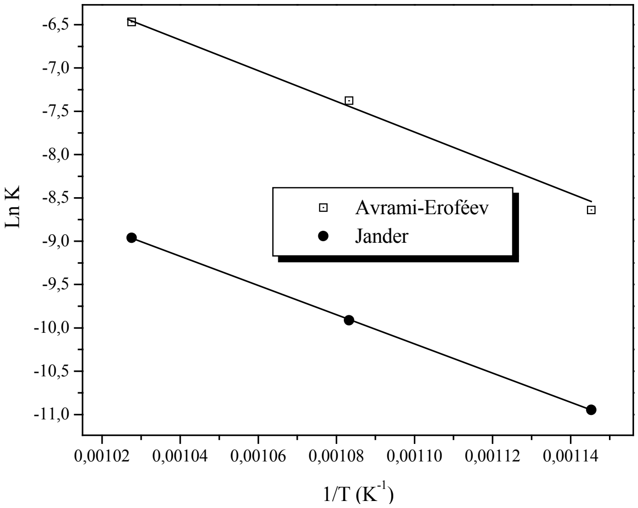

Figure 6. Plots of Ln K or Ln κ vs $1/T$ (Arrhenius expression).

equations used to carry out the standard deviation calculation can be found in any statistics textbook.

Figures 4 and 5 show the experimental fraction of crystallization of δ-$Na_2Si_2O_5$ together with the fits obtained from the Excel-based calculation (using both the Avrami–Eroféev and the Jander expressions). Figure 6 shows a plot of Ln K (in the case of the Avrami–Eroféev expression) or Ln κ for the Jander expression versus $1/T$. With both the Avrami–Eroféev and Jander models there is a significant dependence of the rate constant of crystallization upon temperature (r close to 1, see Table 1).

Table 1 shows the constants and kinetic parameters obtained from each model. For n, Jander´s model reaches a value close to 3, which means that three-dimensional crystal diffusion occurs from nucleation sites. The Avrami–Eroféev expression gives a value close to 0.5; this value is characteristic of processes where the speed of nucleation does not affect the crystal growth. The activation energy obtained by the two models is very similar but there is a difference in the frequency factors. The frequency factor obtained by the Avrami–Eroféev model is higher than that obtained by the Jander expression. This suggests that the crystallization mechanism is faster according to the Avrami–Eroféev model than according to the Jander expression.

Conclusions

Kinetic data can be easily determined by measuring the intensities of reflection of the XRD pattern and can be modeled using the Avrami–Eroféev or Jander expressions. With both expressions, the rate constants and Avrami exponent can be also calculated. By means of the Arrhenius expression, the kinetic parameters, activation energy, and frequency factor can be obtained.

These experiments are useful for chemistry and chemical engineering students and also very pertinent to post-graduate students working in the field of crystalline material synthesis, zeolite for instance, because it shows how to use these two models to calculate kinetic parameters.

Using this process, students learn to calculate the crystallization fraction or degree of crystallinity of materials from experimental data obtained in the laboratory. Once the crystallization fraction is calculated, the instructor can propose several kinetic models to study, discuss which model is the most suitable for understanding the mechanism of crystallization, and finally show how to obtain kinetic parameters from the data.

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