Determination of Growth Kinetics of Polyhedral Crystals

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The kinetics of crystal growth from solution are frequently represented by a simple power-law equation of the form (Mullin, 1972; Garside, 1977)

$$G = K_g(C_b - C_e)^n \tag{1}$$

The growth rate coefficient K_g and the exponent n (sometimes referred to as the "kinetic order") can readily be determined from a log-log plot of linear growth rate G vs. supersaturation $(C_b - C_e)$. The growth mechanism may then be inferred from the value of n and from the dependence of K_g on growth conditions (e.g., temperature, relative crystal/solution velocity). For example, the growth process can be considered to be diffusion controlled if n is equal to one and K_g is influenced by relative crystal/solution velocity. Conversely when n is greater than one and K_g is not influenced by solution velocity, the growth process is most likely controlled by a surface integration mechanism (Mullin, 1972; Garside, 1977).

Mullin et al. (1970) measured face growth rates of single crystals of ammonium sulfate in a flow cell through which supersaturated solution flowed under carefully controlled conditions. They found that the growth rate of the (100) face was first order with respect to the solution supersaturation and was independent of solution velocity. First-order kinetics ($n = 1$) may suggest a diffusion-controlled mechanism, but the lack of a solution velocity effect indicated a surface integration mechanism. Thus, Mullin et al. (1970) concluded that the (100) face growth of ammonium sulfate crystal is not diffusion controlled.

In the application of Eq. 1 to the face growth rates of a polyhedral crystal (i.e., a crystal with different crystallographic faces), the equilibrium saturation concentration C_e associated with a given crystal face is generally assumed to be equal to the nominal solubility associated with the entire crystal. The purpose of this note is to examine the effect of this assumption on the determination of the kinetic order associated with face growth rates of a polyhedral crystal.

For a polyhedral crystal, the equilibrium saturation concentration C_e (often referred to as "solubility") can be different for different crystal faces. Ritzel (1911) reported different solubilities for different forms of NaCl crystals in aqueous solutions. From the measurement of dissolution rates under slightly undersaturated conditions, he obtained a 0.35% difference in solubility between cubic and octahedral NaCl crystals. The concept of different C_e for different crystal faces may be understood by considering the nature of the crystallographic face (hkl) in terms of the value of the "α_{hkl} factor." First defined by Jackson (1958), the α_{hkl} factor represents the degree of surface roughness on an atomic scale and, for the solid/solution interface, can be given by (Bennema, 1979)

$$\alpha_{hkl} = \epsilon_{hkl}\left(\frac{L}{kT}\right) \tag{2}$$

Here ϵ_{hkl} is the crystallographic anisotropy factor, which is different for different faces. L is the differential heat of dissolution, caused by the difference in free energy of solid particles and solute species in a nearly saturated solution.

In general for low values of α_{hkl}, the surface is rough as kink sites are available over the whole surface. As α_{hkl} increases the surface becomes smoother, and at a critical α_{hkl} value ($\alpha_{hkl} \geq 3.2$) the surface becomes flat and smooth on an atomic scale. That is, different crystal faces can have different values of α_{hkl} depending on the nature of crystal surface. Furthermore, based on Jackson's theory of the crystal/solution interface structure (Jackson, 1958), a relationship can be found between the equilibrium chemical potential of a crystal face and its α_{hkl} factor. Thus, the equilibrium chemical potential can be different for different crystal faces, owing to a difference in α_{hkl} values. Since C_e is related to the equilibrium chemical potential (Mullin and Söhnel, 1977), one can, therefore, expect different values of C_e for different crystal faces in a polyhedral crystal.

As mentioned earlier, the equilibrium saturation concentration C_e associated with a given crystal face is generally assumed to be equal to the nominal solubility (here designated by C_s) associated with the entire crystal. To investigate the possible effect of this assumption, we define a parameter $\beta = C_e/C_s$ and determine the kinetic order n as a function of the β values. For $\beta = 1$, C_e is defined to be equal to C_s. For $\beta \neq 1$, the dependence of C_e on the crystal face structure is included in Eq. 1.

In the following analysis, we apply Eq. 1 to the (100) face growth data of the ammonium sulfate crystal reported by Mullin et al. (1970). Using the nominal solubility C_s for the C_e associated with the (100) face (i.e., $\beta = 1$), Mullin et al. (1970) obtained first-order growth kinetics ($n = 1$) from a log-log plot of G versus supersaturation. However, if C_e is considered to be different from C_s (i.e., $\beta \neq 1$) the kinetic order n determined from Eq. 1 would be different from one. This is illustrated in Figure 1, which shows a log-log plot of G versus $C_b - C_e$ for different β values. [The "solubility" C_s of ammonium sulfate in water at 25°C is equal to 0.77 kg/kg water (Mullin et al., 1970.] The kinetic order n increases

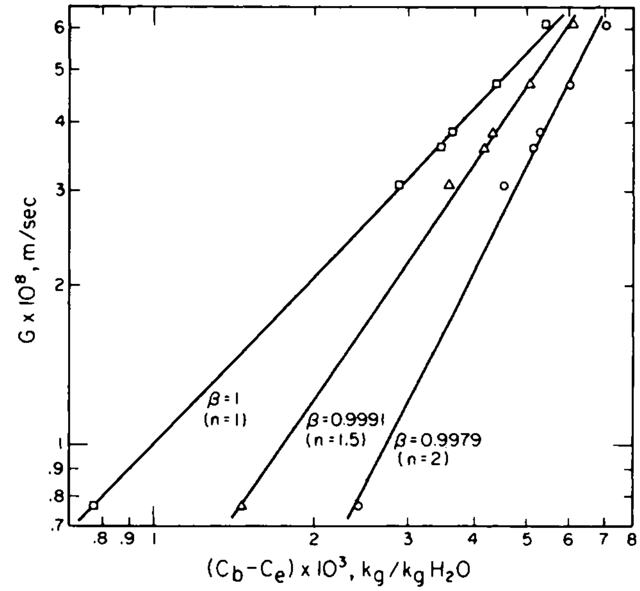

Figure 1. Log G vs, log $(C_b - C_e)$ at different β values for the ammonium sulfate/water system.

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from one to two when β is decreased from one to 0.9979. Values of n smaller than one can also be obtained when β is greater than one.

For $\beta = 1$, the plot in Figure 1 corresponds to that given by Mullin et al. (1970). For $\beta = 0.9991$ and 0.9979, the difference between C_e and C_s is only 0.09% and 0.21%, respectively. Thus, for the ammonium sulfate crystal, the "apparent" kinetic order of the face growth rate is greatly influenced by the accuracy of the C_e value used in the calculation of solution supersaturation. Even with only a 0.21% difference between C_e and C_s, the kinetic order n determined can vary from one to two. This can potentially lead to a wrong interpretation of the growth mechanism. For example, $n = 1$ would suggest a diffusion-controlled mechanism, whereas $n = 2$ would indicate a surface integration mechanism. From a practical point of view, a 0.2% difference between C_e and C_s may be possible for many crystallization systems in light of the 0.35% solubility difference between cubic and octahedral NaCl crystals reported by Ritzel (1911). Therefore, the "correct" C_e value should be used for each given crystal face in order to obtain the "true" growth kinetics. This consideration is particularly important for systems where the supersaturation is small compared to C_e or C_s.

Although the concept of different C_e for different crystal faces has been recognized by Ritzel since 1911, much face growth kinetics reported to date in the form of Eq. 1 (Ohara and Reid, 1973; de Jong and Jančić, 1979) did not consider the different C_e values and hence, may not represent the true growth kinetics. This note points out the potential problems of ignoring the C_e effect and the importance of precise determination of C_e values for different crystal faces. For systems where a precise knowledge of C_e value is lacking, low supersaturation conditions should be avoided to minimize the C_e effect.

In conclusion, the true equilibrium saturation concentration C_e should be used for the determination of the face growth kinetics of a polyhedral crystal. The apparent kinetic order determined can be significantly different from the true value if C_e is replaced by the nominal solubility C_s for the calculation of solution supersaturation.

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NOTATION

C_b = bulk concentration, kg of anhydrous solute per kg of water
C_e = equilibrium saturation concentration associated with a crystal face, $kg \cdot kg^{-1}$
C_s = nominal solubility associated with a given crystal, $kg \cdot kg^{-1}$
G = linear growth rate, $m \cdot s^{-1}$
K_g = growth rate coefficient (Eq. 1)
k = Boltzmann's constant, $J \cdot K^{-1}$
L = differential heat of dissolution, J
n = kinetic order of crystal growth process (Eq. 1)
T = absolute temperature, K
α_{hkl} = α_{hkl} factor (Eq. 2)
β = C_e/C_s
ϵ_{hkl} = crystallographic anisotropy factor

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Film Diffusion-Controlled Kinetics of Isotopic Exchange in a Finite Bath

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INTRODUCTION

It has long been known that the rate of ion exchange between the ion-exchange resins and ions in the liquid solution is controlled by diffusion, either through a hydrostatic boundary layer, call "film diffusion control" or through the pores of the resin matrix, called "particle diffusion control." Under the conditions of small resin particles, dilute solution, and mild stirring, the exchange rate is controlled by film diffusion (Boyd et al., 1947). The rate equation for film diffusion-controlled kinetics of isotopic exchange in a finite bath has been given by Helfferich (1962) and Huang and Tsai (1977) as follows:

$$ln\,(1 - F) = -\frac{3T}{K\delta(1 - U)} \qquad (1)$$

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