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·kg^{-1}
C_s = nominal solubility associated with a given crystal, kg·kg^{-1}
G = linear growth rate, m·s^{-1}
K_g = growth rate coefficient (Eq. 1)
k = Boltzmann's constant, J·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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Equation 1 is derived under the following simplifying assumptions: (1) interdiffusion in the film is treated as quasi-steady state, i.e., it is assumed that diffusion across the film is fast as compared with the concentration changes at the film boundaries; (2) the concentration profile of radioactive isotope in the film is linear; and (3) the amount of radioactive isotope in the film is negligible as compared with that in the resin particles. Assumptions 2 and 3 are admissible if the film thickness is much smaller than the resin radius.

Span (1970) showed that the concentration profile of radioactive isotope in the film becomes nonlinear when the film thickness increases. Furthermore, the amount of radioactive isotope in the film becomes relatively important as compared with that in the resin particles under low stirring speed and low value of distribution coefficient K. Therefore, a general rate equation for film diffusion-controlled kinetics of isotopic exchange in a finite bath is investigated here.

GENERAL SOLUTION

We consider an isotopic exchange process in which the spherical ion-exchange resins are immersed in an agitated solution of finite volume. In treating this isotopic exchange system it is assumed that there is an unstirred liquid film of thickness $b - a$, that a nonlinear concentration profile exists in the film and is described by Fick's second law, that the concentration of radioactive isotope in the bulk solution $C'(t)$ varies with time, and that the diffusion coefficient in the liquid film is constant. The diffusion equation corresponding to such a model is

$$\frac{\partial[rC(r,t)]}{\partial t} = D\frac{\partial^2[rC(r,t)]}{\partial r^2}, a \le r \le b, t > 0 \qquad (2)$$

with the initial and boundary conditions

$$\overline{C}(t) = KC(r,t), r = a, t > 0 \qquad (3)$$

$$\overline{C}(t) = 0, t = 0 \qquad (4)$$

$$C(r,t) = C'(t), r \ge b, t \ge 0 \qquad (5)$$

$$C(r,t) = C'(0), a \le r \le b, t = 0 \qquad (6)$$

$$4\pi a^2 N \int_0^t D\frac{\partial C(r,t)}{\partial r}\bigg|_{r=a} dt = \frac{4}{3}\pi a^3 N\,[\overline{C}(t) - \overline{C}(0)] \qquad (7)$$

$$VC'(0) + \frac{4}{3}(\pi a^3 N\overline{C}(0)$$
$$= \left[V - \frac{4}{3}\pi N(b^3 - a^3)\right] C'(t) + 4\pi N\int_a^b r^2C(r,t)\,dr - \frac{4}{3}\pi a^3 N\overline{C}(t)$$

or

$$V[C'(0) - C'(t)] + \frac{4}{3}\pi N(b^3 - a^3)C'(t) - 4\pi N\int_a^b r^2C(r,t)\,dr = \frac{4}{3}\pi r^3\,[\overline{C}(t) - \overline{C}(0)] \qquad (8)$$

The general solution of these equations can be obtained by the method of Laplace transforms and is given below:

$$F = \frac{M(t)}{M(\infty)} = 1 - 2K\left(1 + \frac{1}{\alpha}\right)\sum_{n=1}^{\infty}\frac{P\,\mathrm{sin}gn + Q\,gn\,\mathrm{cos}gn}{R\,\mathrm{sin}gn + S\,gn\,\mathrm{cos}\,gn}\exp\left(-\frac{gn^2T}{\partial^2}\right) \qquad (9)$$

where $P = -3\delta^2(1+\delta) + [1 + \alpha K + (1+\delta)^3]\,gn^2$

$$Q = 3\delta(1+\delta)^2$$

$$R = 3/\delta^2\,[2(1+\alpha K) + (1+\delta)(4 - 2K + 2\delta + \delta^2)] - \{\alpha K(4K + 3\delta) + 3\delta\,[1 - (1 - K + \delta)(1+\delta)^2] + 4K\,[1 - (1+\delta)^3]\}\,gn^2$$

$$S = 3\delta\,\{(3+\delta)\,[1 + \alpha K - (1+\delta)^3] + (1+\delta)\,[3(1+\delta) \times (K+\delta) - K\delta]\} - K\,[1 + \alpha K - (1+\delta)^3]\,gn^2$$

and gn's are the non-zero roots of the following equation:

$$\frac{gn}{\mathrm{tan}gn} = \frac{9\delta^4(1+\delta) + 3\delta^2(1 + K\alpha - K(1+\delta) + 3(1+\delta)^2 - (1+\delta)^3]\,gn^2 - K[1 + K\alpha - (1+\delta)^3]\,gn^4}{9\delta^4(1+\delta) - 3\delta\,[1 + K\alpha - (1 + \delta - K)(1+\delta)^2]\,gn^2} \qquad (10)$$

The parameter α can be expressed in terms of the final fractional uptake of radioactive isotope by the resin particles, U, by the relation

$$U = \frac{M(\infty)}{VC'(0)} = \frac{1}{1+\alpha} \qquad (11)$$

SIMPLE VS. GENERAL SOLUTION

As can be seen from Eqs. 1, 9, 10 and 11, the relationships between F and T are functions of U, K, and δ for both simple solution and general solution if the isotopic exchange is controlled by film diffusion in a finite volume of solution. From the computed results we find that the infinite series in Equation 9 converges rapidly for large values of T and K and small values of δ and U, and the truncation error is less than 1% at $T = 0$ for any values of U and $K/\delta \ge 200$ if the terms after the first one are excluded from the computation. That is, the relation between $\log(1 - F)$ and T is linear with a slope of $-g_1^2/2.303\,\delta^2$ under $K/\delta \ge 200$, where g^1 is the first root of Eq. 10. While for the simple solution case, this slope is equal to $-3/2.303K\delta(1 - U)$.

Figure 1 indicates the relationships between $\log(1 - F)$ vs. T/δ for $K = 100$ and $U = 0.5$ with δ as parameter. It can be seen that the exchange rate predicted from Eq. 9 is practically coincident with that predicted from Eq. 1 for $\delta \le 0.01$, $U = 0.5$ and $K = 100$. Separate calculations show that for any values of K and U, Eq. 9 agrees well with Eq. 1 when the values of δ are smaller than 0.01. If we transform the coordinates of Figure 1 from $\log(1 - F)$ vs. T/δ to $\log(1 - F)$ vs. T, we can find that the exchange rate increases as the values of δ decrease. It can also be found that the exchange rate predicted from Eq. 9 is faster than that predicted from Eq. 1 at the same values of U, K and δ, and this discrepancy is more obvious as the values of δ increase. At $U = 0.5$, $K = 100$ and $\delta = 0.05$, the time required to reach any values of F based on Eq. 9 is smaller about 5% than that based on Eq. 1.

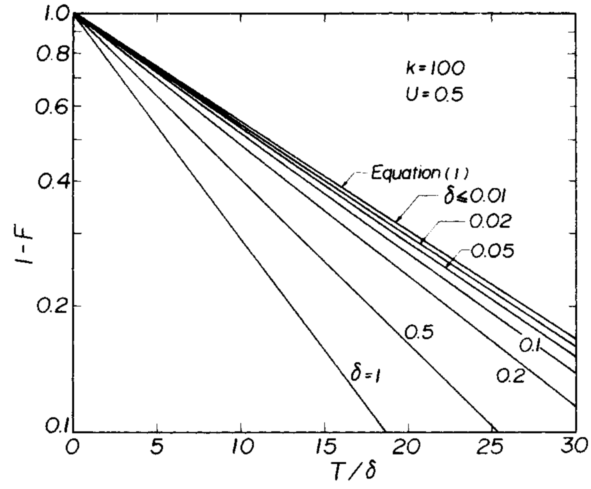

Figure 1. Plots of log(1 − F) vs. T/δ with δ as parameter for $K = 100$ and $U = 0.5$.

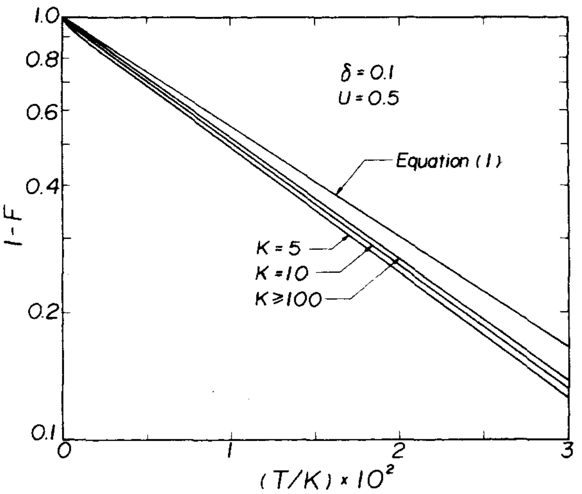

Figure 2. Plots of log(1 − F) vs. T/K with K as parameter for $\delta = 0.1$ and $U = 0.5$.

Figure 2 indicates the relationships between $\log(1 - F)$ vs. T/K for $\delta = 0.1$ and U - 0.5 with K as parameter. It can be seen that the exchange rate predicted from Eq. 9 is always faster than that predicted from Eq. 1 under the conditions of $U = 0.5$, $\delta = 0.1$ and any K values. The discrepancy is about 10% as $K \geq 100$, and is more obvious as the values of K decrease from 100.

Therefore, when the exchange rate is controlled by film diffusion in a finite bath, the exchange rate predicted from Eq. 9 is faster than that predicted from Eq. 1 under large δ and small K.

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NOTATION

a = radius of the resin particle, cm
b = distance from the center of a spherical resin particle to the outer boundary of the liquid film, cm
C = concentration of radioactive isotope in the liquid film, mol/cm^3
C' = concentration of radioactive isotope in the bulk solution, mol/cm^3
$\overline{C}$ = concentration of radioactive isotope in the resin particle, mol/cm^3
D = diffusion coefficient in the solution, cm^2/s
F = fractional attainment of equilibrium
gn = non-zero roots of Eq. 10
K = distribution coefficient
M = total amount of radioactive isotope transferred into the resin particles, mol
N = number of resin particles in the solution
r = distance from the center of a spherical resin particle, cm
t = time, s
T = Dt/a^2
U = final fractional uptake of radioactive isotope by the resin particles
V = volume of the solution, cm^3

Greek Letters

α = $3V/4\pi a^3 NK$
δ = $(b - a)/a$

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Conjugate Unsteady Heat Transfer from a Droplet in Creeping Flow

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Recently, in *AIChE Journal*, Abramzon and Borde (1980) have numerically solved the problem of unsteady heat transfer from a droplet in creeping flow and presented many discussions based on the computed results. Herein, we show that the finite-difference equations used in the above mentioned paper are unstable in part of the region considered.

The problem is to study the unsteady heat transfer from a spherical droplet moving slowly into an unbounded volume of another immiscible liquid. The Reynolds number is taken to be small (Re $\leqslant$ 1) and the flow fields are steady. At time $t = 0$, the temperature of the droplet and of the continuous phase are uniform and are equal to T_o and T_∞ respectively. The physical properties

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