Transport Control in Crystal Growth from Solution

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When a crystal grows or dissolves in a solution the matter has to pass through a diffusion field. If the crystals do not move relative to the surrounding liquid their growth or dissolution rate may be controlled by diffusion through the solution. Crystals of micrometer size or smaller in aqueous solution may be treated as stationary in this respect. For larger crystals also convection may have influence on the growth or dissolution rate. When a crystal grows or dissolves by a transport controlled process no information on the surface processes can be obtained from the empirical kinetics except a lower limit to the rate. As transport processes are more efficient for small crystals than for large ones, as compared to surface processes, there are usually better possibilities for obtaining information about the surface processes when studying small crystals (fine precipitates) than with larger crystalline bodies (rotating discs).

1. INTRODUCTION

A solution has by definition a different composition from that of the crystals — otherwise it would not be a solution but a melt.

When the solute crystallizes the composition of the solution changes (in a closed system), the solution becoming more dilute. The fluxes of the different components from the solution to the crystal are not in the same ratio as the corresponding concentrations in the solution. This shows us that the solute must pass through a diffusion field, where the concentration is lower just outside the crystal than at some distance from it.

If the crystals do not move relative to the surrounding solution, and the average distance to the nearest neighbour crystal is at least of the order of ten diameters (or other longest dimension) the diffusion field around each particle can be approximated — for our purposes — by the stationary field around a spherical sink or source with the same volume as the crystal, and the diffusion controlled rate of growth or dissolution can be calculated by means of this approximating model.1-3

If the crystal moves relative to the solution — because of stirring, sedimentation or thermal convection — the concentration near the crystal becomes closer to the bulk concentration than in the motionless case, the concentration gradient at the surface becomes larger, and the process becomes faster4. This

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is the cause of the well-known effect that stirring may increase the growth or dissolution of crystals. However, this is only the case when the crystals are larger than about 10 µm. Smaller crystals will follow with the moving liquid so that the relative velocity between the crystals and the surrounding liquid (nearer than 2—3 diameters) is negligible.

In chemical kinetics we often classify the elementary steps of an over-all reaction as either parallel or consecutive. The rates of two parallel steps will add, but the rates of two consecutive steps must be equal (when no essential concentration of the intermediate is built up) and the step that would be slowest at equal driving forces determines the rate. Diffusive and convective transport of matter up to a growing crystal (or away from a dissolving one) are both parallel and consecutive. The rate of transport is finite even if convection is completely absent, as with parallel elementary processes. But no matter how fast the convection is, the transport is via diffusion close to the crystal surface (where the liquid velocity relative to the crystal surface converges towards zero, and so the two kinds of transport are also consecutive.

All that comes after the transport up to the crystal surface we shall classify as »surface processes«. This may include adsorption of molecules or ions at the crystal surface — possibly with partial desolvation — migration along the surface within and adsorption layer, adsorption at a step on the surface (at a surface spiral or a two-dimensional surface crystal), twodimensional nucleation, and the final entering into the proper place in the crystal lattice. In case of dissolution the opposite processes will be operating — not to speak of the equilibrium.

For simplicity we shall in the following assume that the suspension of crystals is so well dispersed and »dilute« that the typical or average distance to the nearest neighbour is more than ten times the maximum linear dimension of the individual crystals. For such a suspension one need not distinguish between the bulk or average concentration of the dissolved matter, and the intermediate concentration at points not close to any crystal (not closer than five times the maximum linear crystal dimension). We may also identify these with the concentration at infinite distance which is practical in mathematical calculations where the crystal is assumed to be alone in the middle of an infinite amount of solution.

Transport controlled growth or dissolution rates are always proportional to the difference \( c - c' \) between the bulk concentration and the concentration at the surface, \( c' \). The latter must be clearly distinguished from the concentration in the adsorption layer. The concentration \( c' \) is the limiting concentration in the solution when approaching the crystal surface from the solution side, and stopping just outside the domain of special surface effects such as adsorption layers or electrical double layers. The proportionality between the rate and \( c - c' \) of course presupposes that crystal dimensions, liquid flow, temperature and pressure are all constant. The rate of the surface reaction — and thus of the growth or dissolution — is a function of \( c' \), and any variation of \( c \) will only influence the rate through \( c' \). In some cases \( c' \approx c \) (case I on Figure 1) and the rate is directly governed by the bulk concentration. Then we call the growth or dissolution rate surface controlled. A moderate change of the liquid flow velocity or of the diffusion coefficient (if this were possible) would not by itself influence the rate.
Figure 1. The concentration \( c(p) \) as a function of the distance from the center of a spherical body growing (a), or dissolving (b), in a stagnant solution when the rate is controlled by the surface reaction (I), diffusion (II), or both (II).

The rate must of course converge to zero as \( c' \rightarrow c_s \), the solubility. Quite often the rate is proportional to some power (1 to 3) of the difference \( c' - c_s \), which may be regarded as a measure of the driving force for the surface reaction [other measures of the driving force are \( c'/c_s \) and \( -\Delta \mu_{\text{surf}} = RT \ln (c'/c_s) \)].

Similarly, \( c - c' \) is a measure of the driving force for the transport process [together with \( c/c' \) and \( -\Delta \mu_{\text{rest}} = RT \ln (c/c') \)].

When a crystal grows we have

\[
c > c' > c_s \quad (1.1)
\]

and when it dissolves we have

\[
c < c' < c_s \quad (1.2)
\]

If \( c' \approx c_s \), the rate is transport controlled. This assertion is justified by observing that when \( c - c' \gg c' - c_s \), a moderate relative change of \( c' - c_s \) (say, by a factor of 2) will not change \( c - c' \) appreciably, and therefore not influence the rate either, since this is proportional to \( c - c' \).

When \( c' \) is not much closer to one of \( c \) and \( c_s \) than to the other one, we have an intermediate case (II on Figure 1) with compound transport and surface control. This may be regarded as the general case, those discussed above being extreme cases. By studying the kinetics of transport controlled processes we will become able to separate the influences of the two steps in empirically measured growth or dissolution rate. This will in general be necessary in order to interpret the data in terms of the mechanisms operating in the surface of a crystal during growth or dissolution.

In the following we shall first treat diffusion in a system without macroscopic motion, then convection, the dependence of the rate-determining mechanism on concentration and particle size, and finally the special problems of electrolytes precipitating from a solution where the ionic concentrations are not in the same ratio as in the crystal.
The mathematical treatment of diffusion to or from a body of any other shape than spherical (or ellipsoidal) is much more difficult than the spherical case. As we are in this paper mostly interested in very small precipitate particles, where the information at hand about the crystal habit is usually rather inaccurate, we have no reason for taking the trouble of a very accurate description of the diffusion field. It will be sufficient for us to do the calculation for a spherical model, having the same volume as the actual crystal. Only in case of very thin plates or needles, or strongly branched dendrites we will have to take the errors in consideration. We shall ascribe radii to bodies of any shape, defining the radius as that of a sphere with the same volume.

We will thus in general use the equations

$$v = \frac{4\pi r^3}{3}$$  \hspace{1cm} (2.1)

$$r = \left(\frac{3m}{4\pi \rho}\right)^{1/3} = \left(\frac{3\pi V_m}{4\pi}\right)^{1/3}$$  \hspace{1cm} (2.2)

where $v = $ volume  
$r = $ radius  
$m = $ mass  
$\rho = $ density  
$m = $ amount of matter = $ m/M  
$V_m = $ molar volume = $ M/e  
$M = $ molar mass

In the steady-state diffusion field around a spherical sink or source the concentration gradient is $(c - c')/r$. The tangent at $r' = r$ the curve $c(r')$ versus $r'$ (where $r'$ = distance from the center (see Figure 1)) cuts the vertical $r' = 2r$ at $c(r') = c$, the bulk concentration.

As we shall here study pure diffusion control we insert $c' = c_s$ in the expression for the gradient, and calculate the flux of matter into the spherical crystal by means of Fick's first law:

$$\frac{dn}{dt} = [DA \ \text{grad } c(r')]_r = D \cdot 4\pi r (c - c_s)$$  \hspace{1cm} (2.3)

where $D = $ diffusion coefficient  
$A = $ surface area = $ 4\pi r^2$

Deposition of the amount of matter, $dn$, increases the volume of the spherical crystal by

$$dV = 4\pi r^2 \ dr = V_m \ dn$$  \hspace{1cm} (2.4)

It follows that

$$\frac{dr}{dt} = \frac{V_m}{4\pi r^3} \ dn$$  \hspace{1cm} (2.5)

and

$$\frac{dr}{dt} = \frac{DV_m (c - c_s)}{r}$$  \hspace{1cm} (2.6)
We notice that the linear growth rate $\frac{dr}{dt}$ is directly proportional to the supersaturation $c - c_s$ and inversely proportional to the linear particle size. See Figures 2 and 3.

Figure 2. Diagram for estimating the diffusion controlled rate for given values of radius and concentration difference, $\Delta c = c - c_s$ for growth, $\Delta c = c_s - c$ for dissolution. Valid for $D\nu_m = 5 \times 10^{-14} \text{ m}^2 \text{s}^{-1} \text{mol}^{-1}$, see eq. (2.6).

Figure 3. Nomogram for estimating the diffusion controlled growth or dissolution rate of a spherical particle, according to eq. (2.6).
Equation (2.6) can be integrated for constant concentration. If \( r = 0 \) at \( t = 0 \) we find

\[
  r^2 = 2D V_m (c - c_s) t
\]

or

\[
  r = \sqrt{2D V_m (c - c_s) t}
\]

Equation (2.7) and (2.8) will be valid in the beginning of a precipitation experiment where the radii are small, and the decrease in \( c \) (proportional to \( r^3 \), if the number of crystals is constant) is negligible.

Inserting as typical values \( D = 10^{-9} \text{ m}^2/\text{s} \), \( V_m = 5 \times 10^{-5} \text{ m}^3/\text{mol} \) and \( c - c_s = 10 \text{ mol/m}^3 (= 10 \text{ mM}) \) we find

\[
  r/\text{meter} = 10^{-6} \text{ (t/second)}^{1/2}
\]

or

\[
  r/\mu\text{m} = (\text{t/second})^{1/2}
\]

**TABLE I**

<table>
<thead>
<tr>
<th>( t = 0.01 \text{s} )</th>
<th>( 1 \text{s} )</th>
<th>( 100 \text{s} )</th>
<th>( 10% (= 2.8 \text{h}) )</th>
<th>( 10^6 \text{s} (= 11.6 \text{d}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r = 0.1 \mu\text{m} )</td>
<td>( 1 \mu\text{m} )</td>
<td>( 10 \mu\text{m} )</td>
<td>( 100 \mu\text{m} )</td>
<td>( 10^4 \mu\text{m} (= 1 \text{mm}) )</td>
</tr>
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One of the important assumptions was that the diffusion field around a growing spherical particle could be approximated by the steady-state diffusion field. This can be tested by using that any steady-state diffusion field has a relaxation time of the order of \( \tau \approx x^2/2D \) when \( x \) is a characteristic linear dimension of the field. Using \( x = r \) we find

\[
  \tau = \frac{r^2/2D}{4} = \frac{r^2/2D V_m (c - c_s)}{4} = V_m (c - c_s)
\]

With the typical values used before we find

\[
  \tau/t = 5 \times 10^{-4}
\]

As the relaxation time is less than one thousandth of the actual age of the system, the approximation must be good.

The product on the right-hand side of (2.11) appears in so many equations for diffusion controlled growth and dissolution that we should realize its nature. The factor \( c - c_s \) is the amount of matter that could be precipitated from a unit volume, so \( V_m (c - c_s) \) is the volume of the precipitate that could be formed from a unit volume of the solution, when the concentration decreases to the saturation value. \( V_m (c - c_s) \) is thus equal to volume fraction of the solute that is present in the solution, in excess to the solubility.

Similarly, in case of an undersaturated solution \( V_m (c - c) \) is the volume fraction that corresponds to the amount of matter that can be dissolved before saturation is reached. Above we integrated the rate-equation for constant bulk concentration. If a precipitate is formed in a closed system the solution is gradually depleted, and as \( c \to c_s \), the rate decreases. In many experiments
it is a good approximation to say that all the crystals are formed simultaneously (at $t = 0$) and grow with the same rate. Introducing $\alpha$,

$$\alpha \equiv (r/r_f)^3 = \frac{c_0 - c}{c_0 - c_s}$$  \hspace{1cm} (2.12)$$

where $\alpha$ is the degree of reaction, $0 \leq \alpha(t) \leq 1$

$$r_i = r$ for $\alpha = 1$ \hspace{1cm} (t = \infty)$$

$$c_0 \equiv c$ for $t = 0$$

we may integrate (2.6) to obtain\textsuperscript{8,9,18}

$$k_0 t = \int_{0}^{a} \alpha^{-1/3} (1 - \alpha)^{1} \, d\alpha' = I_0(\alpha)$$ \hspace{1cm} (2.13)$$

where \n
$$k_0 = \text{rate constant} = 3 DV_m(c_0 - c_f)/r_1^2$$ \hspace{1cm} (2.14)$$

and where $I_0(\alpha)$ is a function of $\alpha$ (a dimensionless time, or chromatom\textsuperscript{19}). Values of $I_0(\alpha)$ may be obtained from the nomogram, Figure 10.

Eq. (2.14) may be transformed into

$$k_0 = D \left[ 48 \pi^2 V_m (c_0 - c_f) N^1/3 \right]$$ \hspace{1cm} (2.15)$$

where $N$ is the particle number density.

$N$ may be measured by counting the number of crystals formed in a known volume, and dividing the number by the volume. The counting may be performed by means of a light microscope and a blood cell counting plate, or with a slide with accurately known spacing between slide glass and cover glass, using an eye-piece chequered grid, or by an automatic counting device such as a Coulter Counter.

If the precipitation experiment is started at $t = t_0$ by adding a mono-disperse sample of seeds to a supersaturated solution, we may express the dependence of $c$ on time by

$$k_0 (t - t_0) = I_0(\alpha) - I_0(\alpha_0)$$ \hspace{1cm} (2.16)$$

where $\alpha$ is defined by

$$\alpha \equiv \frac{c_0 - c}{c_0 - c_s}$$ \hspace{1cm} (2.17)$$

where $c_s$ includes the total amount of matter in the seeds, just as if it hypothetically had been homogeneously dissolved to give $c = c_s$ at some time $t_s < t_0$.

In the classical homogeneous kinetic method in chemistry one measures $c$ or $\alpha$ as a function of time (a progress curve) and checks the hypothesis by plotting some appropriate function of $c$ or of $\alpha$ as a function of $t$, [ln $(1 - \alpha)$ for a first order reaction, and $1/c$ for a second order reaction]. In exactly the same manner one may test whether a precipitation process is purely diffusion controlled by plotting $I_0(\alpha)$ as a function of $t$. A straight line verifies the hypothesis. Actually we are in a better situation than normally in chemical kinetics, because we know in advance what the correct value of the rate-con-
stant would be, as it can be calculated from Eq. (2.14) or (2.15), where all parameters are either known or may easily be obtained from the experiment independent of the kinetic data.

In this way we have a double check of the diffusion control hypothesis. There is no excuse for relying on more questionable arguments such as whether the rate is stirring sensitive (which only applies to crystals so large that they do not go with the stream under stirring) or whether the activation energy happens to be the same as calculated from the dependence of \( D \) on temperature. One should make it clear that for the estimate of \( k_b \) even a very crude determination of \( r_1 \) or of \( N \) will be sufficient, because the rate will typically be only 0.1 or less of the diffusion controlled rate, when a surface reaction is rate controlling.

There may be several reasons for not making a \( t, I_D (\alpha) \) plot, but usually the half-life period may be easily deduced from empirical data. The first half life period \( t_{1/2}^0 \) (the length of the period from \( \alpha = 0 \) to \( \alpha = 1/2 \)) may be expressed by inserting \( I_D (0.5) = 1.2290 \) and \( k_D \) into equation (2.13)

\[
t_{1/2}^0 = \frac{1.2290}{k_D}
\]

By rearranging, and using (2.14) we find

\[
D = \frac{0.4097 r_1^2}{V_m (c_o - c_s) t_{1/2}^0} = \frac{0.1577}{[V_m (c_o - c_s) N^2]^{1/4}}
\]

(2.19)

In practice one will often measure the particle diameter \( d \) instead of the radius \( r \), and \( V_m (c_o - c_s) \) will be calculated as

\[
V_m (c_o - c_s) = \frac{v}{V} = \frac{m}{q V}
\]

(2.20)

where \( v \) = volume of the precipitate at \( \alpha = 1 \),

\( V \) = volume of the suspension,

\( m \) = mass of the precipitate at \( \alpha = 1 \),

\( q \) = density of the crystals.

Inserting \( d \) and (2.18) the first equation in (2.19) is modified into

\[
D = 0.1024 \frac{q V}{m} \cdot \frac{d^2}{t_{1/2}^0}
\]

(2.21)

where \( d = 2 r_1 \).

Towards the end of the precipitation experiment, when \( \alpha \approx 1 \) the particle dimensions vary little, and the rate becomes proportional to \( c_o - c_s \). The variation of \( \alpha \) (or \( c \)) with time will consequently be as in a homogeneous first order reaction, and the half-life period becomes constant. For the limiting value \( t_{1/2}^{\infty} \) we have

\[
D = 0.05776 \frac{q V}{m} \cdot \frac{d^2}{t_{1/2}^{\infty}}
\]

(2.22)

where \( 0.05776 = (\ln 2)/12 \).
The equations (2.21) and (2.22) can also be applied if the precipitate is polydispersed (consists of particles of different sizes). In that case the »average« value of \(d^2\) to be used is

\[
d^2 = \frac{\sum d_i^3}{\sum d_i}
\]  (2.23)

The equations (2.22) and (2.23) can furthermore be applied on data obtained from a seeded precipitation reaction, and from a dissolution experiment with excess solute.

3. INFLUENCE OF CONVECTION

When a crystal (or any other solid body) is moved in a large volume of liquid which is everywhere at rest except locally near the moving body, the velocity \(u\) of the liquid relative to the body varies gradually from \(u = 0\) in the liquid closest to the interface to \(u = U = a\) constant at great distance from the crystal. The greatest change of \(u\) takes place close to the crystal, within a distance of the order of the linear dimension (radius) of the crystal.

In the preceding section we noted that a growing or dissolving particle established a steady-state diffusion field around itself in a period of time of the order of \(T = r^2/2D\) — when the liquid is stagnant. When the liquid is moving relative to the crystal (or vice versa) the diffusion field will be perturbed, but for sufficiently small bulk velocities \(v\) the perturbation will have a vanishingly small influence on the growth rate.

The flow rate at which the perturbation becomes essential (changing the rate by say 50\%) will be of the order of the flow rate that renews the liquid in the diffusion field (of thickness of the order \(r\)) around the crystal in a period of the length, \(\tau\). We estimate that the liquid is essentially (ca. 50\%) renewed when the displacement is one radius, and conclude that this happens when the velocity is about

\[
U = \frac{r}{\tau} \approx \frac{r^2/2D}{r} = \frac{2D}{r} \approx \frac{D}{\tau}
\]  (3.1)

The relative velocity between a falling sphere of radius \(r\), and the surrounding liquid was found by Stokes (for Reynolds number, \(2 r U \rho/\eta < 1\)) to be

\[
U = \frac{2 a \Delta \rho \rho r^3}{9 \eta}
\]  (3.2)

where \(a\) = acceleration,

\(\Delta \rho\) = density difference crystal-liquid,

\(\eta\) = dynamic viscosity.

For a resting suspension, and even for a moderately stirred suspension \(a = g = 9.8\ m/s^2\), the acceleration of gravity. For vigorous stirring and for centrifugation \(a\) will be larger than \(g\).

By equating \(U\) from (3.1) and from (3.2) we find the radius \(r_{CD}\) at which convection begins to have essential influence on diffusion controlled growth rates.
Figure 4 shows values of $r_{CD}$ for crystals of different densities $\rho$ in aqueous solution (density $\rho_0$). When $\rho = \rho_0$, the sedimentation velocity becomes zero, and crystals of any size become motionless and develop a stagnant, steady-state diffusion field. The dimensionless ratio

$$r^2 r_{CD}^3 = \frac{2 a r^2 \Delta \rho}{9 D \eta} = \text{Pe}^*$$

is called the Peclet number for mass transfer. For $r < r_{CD}$ ($\text{Pe}^* < 1$) the rate is only influenced moderately or negligibly by convection, and for $r > r_{CD}$ the diffusion controlled rate is enhanced by the convection.

Quantitatively, the influence of convection on the otherwise diffusion controlled growth or dissolution rate may be expressed by

$$\frac{dr}{dt} = \left(\frac{dr}{dt}\right)_o \cdot F$$

where

$$\left(\frac{dr}{dt}\right)_o = \frac{D V_m (c - c_o)}{\tau}$$

is the diffusion controlled rate in a stagnant liquid (eq. (2.6)) and where $F = F(U, \text{etc}) \to 1$ for $U \to 0$. 
CRYSTAL GROWTH FROM SOLUTION

In the engineering literature, $F$ is expressed by the equation

$$ F = 1 + 0.3 \frac{Re}{Sc} \frac{Sc}{Re} \quad (3.7) $$

where

$$ Re = \text{Reynolds number} = 2 \frac{\rho U \delta}{\eta} (3.8) $$

$$ Sc = \text{Schmidt number} = \frac{\eta D}{\nu} \quad (3.9) $$

We notice that $Pe* = 1/2 Re Sc$, and that in aqueous solution at ambient temperature — assuming the diffusing species is not macromolecular — the Schmidt number is always of the order $10^3$, so that $Pe* \approx 500 Re$. By numerical solution of the hydrodynamic equations for $Pe* < 10^3$ we found a presumably more accurate equation for $F$

$$ F = (1 + Pe*)^{0.25} \quad (3.10) $$

If we express the dependence of $dr/dt$ or $r$ — other factors being constant — by

$$ \frac{dr}{dt} = r^* \quad (3.11) $$

then all equations agree that for transport controlled growth or dissolution $n = -1$ for $Pe* \ll 1$

For $Pe* \gg 1$, however, $F_R$ leads to $n = 1.50$ and $F_N$ to $n = 0.855$. So far we have treated diffusion controlled growth or dissolution where the growth rate was increased by the motion of the crystals relative to the liquid caused by sedimentation in the field of gravity or a centrifuge. These results will also apply in case of moderate stirring. But if the suspension is vigorously stirred, even greater growth rates will be obtained. According to Levich, one must distinguish between two cases, $r \ll \lambda_o$ and $r \gg \lambda_o$ where $\lambda_o$ is the microscale of turbulence, $\lambda_o = L/Re^{3/4}$ where $L$ is a typical scale of the motion, such as container diameter, and where $Re$ is the Reynolds number for the the total system, $Re = \frac{UL}{\nu}$, and $U$ = over-all velocity of the liquid. For $r \ll \lambda_o$

$$ \frac{dr}{dt} = 0.46 \left( \frac{\rho}{\rho_0} \right)^{1/3} \frac{D}{\eta} \left( \frac{\rho}{\rho_0} \right)^{1/2} L^{3/4} V_m U^{1/4} (c - c_f) \quad (3.12) $$

and for $r \gg \lambda_o$

$$ \frac{dr}{dt} = 1.26 \left( \frac{\rho}{\rho_0} \right)^{1/4} L^{-1/4} V_m U (c - c_f) \quad (3.13) $$

In the last case, of extremely vigorous stirring, $D$ does not appear in the expression which means that we have purely convection controlled growth (assuming the surface processes can still keep the pace!).

The Unstirred Layer Model

As mentioned before, the local velocity, $u$, of the liquid relative to the crystal changes gradually from $u = 0$ at the crystal surface to $u = U$ at great distances from the crystal. Nevertheless many people adhere to a model assuming that the liquid closer than some distance $\delta$ from the surface...
forms an immobile layer, yet with the usual bulk liquid diffusion coefficient for the diffusing solute molecules or ions. The model does not clearly describe the liquid flow outside the unstirred layer of thickness \( \delta \), but it assumes that the concentration is the bulk concentration at the distance, \( \delta \). Strictly speaking this can only be so (during growth or dissolution) if there is a most violent turbidity just outside the unstirred layer. However, as the liquid velocity does not enter explicitly in the equations we may courteously neglect this problem. The advantage of this model is that it gives a simple expression for the concentration gradient at the crystal surface,

\[
\text{grad} \ c = \frac{c - c_0}{\delta}
\]

leading, via Fick's first law, to the rate expression

\[
\frac{dr}{dt} = \frac{D V_m (c - c_0)}{\delta}
\]

Comparing with 3.5 and 3.6 we find

\[
\delta = \frac{r}{F}
\]

showing that for small crystals

\[
\delta = r \quad (r \ll r_{CD}, F \approx 1)
\]

and for larger crystals

\[
\delta = \frac{r}{(1 + Pe^*)^{0.883}} \sim \frac{r}{r^{0.855}} = r^{0.145}
\]

In this range an increase of \( r \) by the factor \( 10 = 1000\% \) will only increase \( \delta \) by the factor \( 10^{0.145} = 1.40 \), or \( 40\% \). This effect explains that the unstirred layer theory has become so popular: \( \delta \) is a reasonably constant fitting parameter for \( r \gg 10 \mu m \).

To clarify this point we have plotted \( \delta \)-values calculated for crystals of density \( \rho = 3 \times 10^3 \text{ kg/m}^3 \) in aqueous solution \( (\rho_l = 10^3 \text{ kg/m}^3, D = 10^{-9} \text{ m}^2/\text{s}, \eta = 10^{-3} \text{ Pa} \cdot \text{s}, a = g = 10 \text{ cm/s}^2) \) in a logarithmic diagram, Figure 5.

4. SEEDING AND »ROTATING DISC«

When a precipitation experiment is started by forming a homogeneous supersaturated solution so that the crystals come »by themselves« through a heterogeneous or homogeneous nucleation one may be lucky to get a quite uniform population of crystals, but more often they vary in size and shape, and the number formed may be rather irreproducible. This complicates the numerical treatment of the data obtained, and irreproducibility is, of course, a fundamental shortcoming in exact science. There are several ways to overcome this problem. One is just to choose a way of treating the data so that the influence of the variations are either eliminated, using proper models or empirical corrections — or one may even take advantage of the scattering considering it as a wellcome variation of the experimental parameters that should otherwise have been provoked by some means.
Figure 5. Logarithmic plot of the thickness, $\delta$, of the 'unstirred layer' as a function of the particle radius for a crystal falling through an aqueous solution at ambient temperature. $E$ = from engineering practice, $N$ = from numerical solution of the hydrodynamic equations. The indices on $E$ and $N$ indicate the density difference in kg/dm$^3$. For $\Delta\rho = 0$ the system is motionless and $\delta$ is equal to $r$ for any size.

Some investigators, on the other hand, do a great piece of work to obtain reproducible experiments by preparing a large stock of reasonably uniform seed crystals, large enough to be measured accurately, and strat the experiments by first making a supersaturated solution that would be stable for some time if the seeds were not added — and then initiate the kinetic part of the experiment by adding a portion of the seeds. But this method has also its shortcomings. First of all, it restricts the values of concentrations for which the crystal growth kinetics may be investigated to a rather narrow range close to the solubility. It also sets a lower boundary to the sizes of crystals tested. And the influence of adsorbed impurities may be more serious.

In planning a precipitation experiment it is often advisable to realize that, generally speaking, one usually has

$$\frac{dr}{dt} = k_s (c' - c)_s = \frac{DV_m (c - c')}{r} = k_s (c - c')^p$$

(4.1)

[If $r > r_{cd}$ the last term should be multiplied by $F$ (eq. 3.10)] where $p > 1$. We may — still speaking about the gross features — claim that the growth rate is surface controlled when $c' - c_s > c - c'$ and diffusion controlled for the opposite inequality. The change-over line in a $c$, $r$-coordinate system is found by letting $c' - c_s = c - c'$, solving, and eliminating $c'$.
\[ k_s (c - c')^p = \frac{DV_m}{r} (c - c') \]  
\[ c - c' = c' - c_s = \left( \frac{DV_m}{k_s r} \right)^{1/p} \]  
\[ c - c_s = 2 \left( \frac{DV_m}{k_s r} \right)^{1/p} \]  
\[ \tau = \tau_{TS} = \left( \frac{k}{c - c_s} \right)^{p-1} \]  
\[ \tau = \tau_{TS} = \left( \frac{k}{c - c_s} \right)^{p-1} \cdot F \]

For \( p > 1 \) the curve, \( r \) as a function of \( c \), resembles a hyperbola with the asymptotes \( r = 0 \) \( c = c_s \). In the plot, Figure 6, the diagram \([c, r] \) is divided into four parts. In I and II crystals dissolve and in III and IV they grow. Furthermore, in I and IV the processes are diffusion controlled and in II and III they are surface reaction controlled.

Consequently, if we are interested in measuring diffusion coefficients, we shall plan experiments with large crystals and large under- or supersaturation, and if we are interested in studying surface processes, we shall choose small crystals, and concentrations not too far from the solubility — the smaller the crystals are, the greater is the concentration range where we can study surface controlled processes.

The areas marked A and B show where seeded experiments can be performed. Growth kinetics can only be studied above \( r_{seed} \) and to the left of the

**Figure 6.** Diagrams showing the areas in a \( c,r \)-coordinate system where the following mechanisms are dominating:

- I, diffusion controlled dissolution; II, surface controlled dissolution; III, surface controlled growth; and IV, diffusion controlled growth. The curves correspond to fixed values of the ratio, \( c - c' \) to \( c' - c_s \), for instance the ratio 1:1. In Figure 6 a, b, and c the diagram has been plotted for \( p = 2 \) (see eq. (4.1) and (4.4)). \( r_{TS} \) is the value of the radius (as a function of \( c \)) where transport (diffusion) and surface processes are equally important. \( c_{het} \) is the metastability limit, or the critical concentration for heterogeneous nucleation, and \( c_{hom} \) is the critical concentration for homogeneous nucleation.
In Figure 6b are shown the areas where it is possible to use different experimental methods. A, dissolution of crystals (seeds); B, growth of seed and of nucleated crystals; C, growth of crystals nucleated in the system, but not of seeds; D, area of homogeneous nucleation — "pure" growth experiment are normally not possible here.

In Figure 6c are plotted curves for different values of the ratio mentioned above, defining "percent diffusion" as \( \frac{100(c - c')}{(c - c_s)} \). In Figure 6d is shown the kind of diagram corresponding to \( p = 1 \), and in Figure 6e a diagram with \( p = \frac{1}{2} \).

The area D is inaccessible for growth studies because of fast homogeneous nucleation. In Figure 6 are also shown "lifelines" for monodisperse crystal populations for which the mass balance may be written

\[
r^2 + K_1(c - c_s) = K_2
\]  

This in a straight line in a \( c, r^2 \)-coordinate system, but a hyperbola of third order in the \( c, r \)-system. Four examples of life-lines are shown 1) dissolution in excess solvent, 2) dissolution of excess solute, 3) seeded growth and 4) nucleated growth. The examples were chosen so that it could be that the seeds for experiments no. 1, 2 and 3 were produced in experiment no. 4.

For investigators who insist in using seeds there is a possibility for expanding the concentration range and still remain within the area of surface control-
led growth or dissolution: They may stir the solution or move the crystal so strongly that convection speeds up the transport process (and lowers the value of $\delta$). A certain experimental set-up with the crystalline material placed in a rotating disc has become widely used.

It turns out\textsuperscript{14} that the efficiency of the transport up to a rotating disc can be expressed by the (apparent) thickness of the unstirred layer, $\delta$, in the sense that the rate of transport is as over a distance $\delta$ with the concentration gradient $(c - s)/\delta$. The $\delta$-value is a function of — among other things — the rotational speed, but not of the distance from the rotation axis. For aqueous solution at ambient temperature.

$$
\delta = K \cdot \nu^{1/3}, \quad K = 70 \mu m \ m/s^{1/3}
$$

where $\nu$ is the number of rotation per second. We deduce that in order to obtain an efficiency corresponding to $\delta = 10 \mu m$ the disc must do 50 rotation per second. The same efficiency could be obtained with crystals (seeds) in the 20 $\mu m$ range falling by gravity through the solution, and still smaller seeds (or crystals nucleated in the beginning of the precipitation experiment) would be even more efficient. Thus the rotating disc apparatus — which is excellent for measuring, for instance, the empirical rate of dissolution of pharmaceutical products under reproducible conditions — is in general not the best apparatus for the study of surface processes.

5. ELECTROLYTE CRYSTALLIZATION FROM NON-STOICHIOMETRIC SOLUTION

In the previous treatment we have everywhere assumed that the composition of the solution could be described by one parameter, $c$, and that saturation corresponds to a certain value, $c_s$, of this parameter. This is the case with crystals forming only one molecular species when dissolved, such as simple molecular compound. But if the solute in the solution consist of more than one species, such as electrolytes, double salts, metallic compounds or crystallization compounds the «concentration» of the solute becomes a »vector» — meaning that it consists of several independent parameters. If a binary electrolyte grows by a transport controlled rate at large excess of one of the ionic species, the rate will be almost independent of concentration of the excess component, the rate determining step being the transport of the deficient ionic species.

The equations describing the general case for a binary compound have been presented before\textsuperscript{8,15}. For two components A and B with the concentrations $a$ and $b$, the diffusion coefficients $D_A$ and $D_B$ and the solubility product $K$ we found

$$
\frac{dr}{dt} = \frac{V_m}{2\tau} [a D_A + b D_B - \sqrt{(a D_A - b D_B)^2 + 4 D_A D_B K}]
$$

if $D_A = D_B \equiv D$ the expression is simplified to

$$
\frac{dr}{dt} = \frac{V_m}{2\tau} \sqrt{a + b - \sqrt{(a - b)^2 + 4 K}}
$$

It is easy to see that if $(a - b)^2 \gg 4 K$ this becomes
Expressing \( b \) as a function of \( a \) for constant \( dr/dt \) we find the equation for an *isotach*, a curve for constant rate. An example is plotted in Figure 7 which has been published before together with more details.

![Image](image.png)

**Figure 7.** Isotachs (contour lines for constant growth rates) for purely diffusion controlled growth of crystals of a symmetric binary compound \( AB \), which in the solution is completely dissociated in molecules \( A + B \), or ions \( A^{+} + B^{-} \).

When growth data are being analysed in order to find out what is going on in molecular scale, one of the first steps will usually be to decide how great influence on the rate diffusion — or, in general, transport has on the growth rate measured. In principle this may be done by calculating the theoretical transport controlled rate and compare it with the empirical rate. This would be rather complicated if we should base the calculations on the actual shapes of the crystals. Instead we calculate the rate for a sphere of the average volume of the crystals of the experiment, and compare this with the measured rate taking into regard that aspheric crystals may grow some 2—5 times as fast as spheric ones. We have done this for barium sulphate, and found it convenient to calculate the ratio \( q = \frac{r}{r_{0}} \) between the empirical rate and the »spherical« diffusion controlled rate, see Figures 8 and 9. Comparing Figure 8 with Figure 7 we see that the empirical isotachs qualitatively follow the theoretical ones for diffusion controlled growth. From Figure 9 it is clear that the agreement is quantitatively good only where the barium and sulphate ion concentrations are equivalent and high. For dilute solution (upper right-hand corner) the rate is considerably less than the diffusion controlled rate, indicating that it is surface controlled. At high off-equivalent concentrations the rate is 2—5 times larger than the »spherical« diffusion controlled rate. Just in these regions the particles are far from spherical — they are rather branched or dendritic and we may conclude that it is most likely that the growth rate is due to asphericity. Consequently we cannot get any informat-
Figure 8. Experimental isotachs for barium sulphate precipitation in aqueous solution at 25 °C. The symbol \( \tau \) means d\( \tau \)/dt, where \( \tau \) is the radius of a sphere with the same volume as a crystal (population average).

Figure 9. The ratio experimental rate \( (r) \) to calculated diffusional controlled rate \( (r_0) \) of a sphere of radius \( r \). Values smaller than 1 are explained as due to surface control; values larger than 1 may be due to the dendritic shape of the particles at high concentration.

6. (APPENDIX I) DIFFUSION COEFFICIENTS OF IONS AND ELECTROLYTES

In chemical kinetics one can usually predict from a given hypothesis how the rate will vary with the concentrations, but it is in general much more difficult to predict the absolute value of the rate. This also holds good for the surface processes in crystal growth and dissolution kinetics. But for transport control one can in general predict both the dependence of the rate on concentration and crystal size, and the absolute value of the rate. This is because all diffusion phenomena can in principle be solved by means of
Fick's laws using known values for the diffusion coefficients, and these can be measured independent of the growth or dissolution process. In practice, however, diffusion coefficients of sparingly soluble substances may be difficult to obtain directly because of the very small concentrations that can be realized in the diffusion cell. With electrolytes there is a generally applicable way to solve the problem, because the diffusion coefficients of single ionic species can be calculated from the molar ionic electric conductivities by means of the Nernst equation:

\[ D_i = \frac{RT}{F^2} \frac{\Lambda_i}{z_i^2} \]  

(6.1)

where \( D_i \) = ionic diffusion coefficient, \( R \) = gas constant, \( T \) = temperature, \( F \) = Faraday constant, \( \Lambda_i \) = molar ionic electric conductivity (S. I. unit S m\(^2\) mol\(^{-1}\)), \( z_i \) = electric charge number.

(Example: At 25 °C, \( \frac{RT}{F^2} = 2.6627 \times 10^{-7} \) J mol C\(^{-2}\), \( D_{Na}^{+} = 2.6627 \times 10^{-7} \times \times 0.01190/4 = 7.92 \times 10^{-10} \) m\(^2\)/s)

When a binary electrolyte is the only solute present in the solution the ionic concentrations must everywhere in the solution have the same ratio as in the solid, because of the principle of electroneutrality. And when the ions migrate in a concentration gradient or electric field the fluxes must also be in the same ratio, and consequently both the ionic species migrate with the same velocity.

In general the different ions have different mobilities. The mechanism that forces them to go by the same velocity is the same as that of the diffusion potential: As soon an (analytical immeasurable) quantity of the more mobile ions has got the lead their charges will set up an electric field that retards them just enough to follow the less mobile ions. The total electrolyte thus migrates as a single component solute, and the corresponding diffusion coefficient was found by Nernst to be the harmonic mean of the diffusion coefficients of the two ionic species. For a symmetric electrolyte AB

\[ D_{AB} = \frac{2 D_A D_B}{D_A + D_B} \]  

(6.2)

and for a binary electrolyte in general, \( A_\alpha B_\beta \) which dissociates completely into \( \alpha A^{z_+} + \beta B^{z_-} \) \((\alpha z_+ = \beta z_-)\)

\[ D_{\alpha A^{z_+} \beta B^{z_-}} = \frac{(\alpha z_A + \beta z_B) D_A D_B}{\alpha z_A + \beta z_B} = \frac{(\alpha + \beta) D_A D_B}{\beta D_A + \alpha D_B} \]  

(6.3)

When an electrolyte with more than two kinds of ions diffuses the more mobile of two ionic species with the same charge will migrate faster than the other one. Therefore the diffusion of a ternary or quaternary etc. electrolyte cannot be described as a single solute diffusion, and no diffusion coefficient for the electrolyte as the whole can be defined. However, when the utmost precision is not attempted, the process may be approximately described as a single com-
ponent diffusion, with a diffusion coefficient calculated by the expansion of the first of the two equations (6.3) adding $z_c + z_p \ldots$ in the paranthesis and $z_c D_c + z_p D_p \ldots$ in the denominator, but the more ionic species present the more freely do they diffuse, and the more should the slowest species be weighted. In the presence of a large excess of indifferent electrolytes the diffusion potential in quenched, and the best approximation may be

$$D_{A,B,C} = D_{\text{min}}$$

(6.4)

where $D_{\text{min}}$ is the smallest among $D_A$, $D_B$ and $D_C$.

A case of special interest (with a symmetrical electrolyte $AB$) is growth in a solution with $a = b$, but with quenched diffusion potential. From equation 5.1 follows

$$\frac{dr}{dt} = \frac{V_m a}{2r} [D_A + D_B - \sqrt{(D_A - D_B)^2 + 4 D_A D_B K/a^2}]$$

(6.5)

If we try to express this as for a one-component diffusion

$$\frac{dr}{dt} = \frac{DV_m a}{r} \left[ \left( \frac{1 - a_s}{a} \right) \right]$$

(6.6)

we find that

$$D = D_A + D_B - \sqrt{(D_A - D_B)^2 + 4 D_A D_B K/a^2}$$

(6.7)

which depends on the concentration, $a$. For high supersaturation, $a \gg \sqrt{K}$ we may insert $K = 0$, and find

$$D = \frac{D_A + D_B - |D_A - D_B|}{2} \left\{ \begin{array}{l} = D_B (D_A > D_B) \\ = D_A (D_A < D_B) \end{array} \right\}$$

(6.8)

The apparent diffusion coefficient will thus be the smaller of the two single ionic diffusion coefficients. In this extreme case ($K = 0$) the concentrations at the crystal surface are

$$b' = 0, \ a' = a \left( \frac{D_B}{D_A} \right) (D_A > D_B)$$

(6.9)

$$a' = 0, \ b' = b \left( \frac{D_A}{D_B} \right) (D_A < D_B)$$

(6.10)

We have here only treated relatively simple cases. For a more general treatment we may refer to the work of Wilcox[17]. Even in relatively simple cases the exact calculation of compound diffusion coefficients may give rise to several problems. Not to speak of the dependence on ionic strength.

But in crystal growth there are often so many sources of errors or uncertainties (for instance the description of the shape — which we have everywhere in this paper approximated by a sphere) — that one will manage quite well with the rule-of-thumb value for all molecular and ionic species of molecular weight less than 1000, $D \approx 10^{-9}$ m$^2$/s, excepting of course $H^+$ and $OH^-$ which diffuse respectively 10 and 5 times as fast.
CRYSTAL GROWTH FROM SOLUTION

7. (APPENDIX II) DIFFUSION CONTROLLED DISSOLUTION

We consider the diffusion controlled dissolution for a suspension of equally large spherical solid particles following the rate equation (2.6), the system being closed.

We have as before \( c = \) actual bulk concentration, \( c_s = \) the value of \( c \) at solubility equilibrium. Furthermore we defined \( c_s \) as the concentration corresponding to all the solid being dissolved. The degree of reaction is defined by

\[
\alpha = \frac{c}{c_s} \quad (7.1)
\]

and the hypothetic final value of \( \alpha \) if all the solid were dissolved is

\[
\alpha_\infty = \frac{c_f}{c_s} \quad (7.2)
\]

For simplicity let \( c = 0 \) at \( t = 0 \). The particles are assumed to remain spherical at all times, with the radii

\[
\tau = \tau_0 \left( 1 - \alpha / \alpha_\infty \right)^{1/3} \quad (7.3)
\]

where \( \tau_0 \) is the value of \( \tau \) at \( t = 0 \). If the number density of the particles is \( N \), we have

\[
\alpha_x = \left( 4 \pi / 3 \right) \tau_0^3 N/V_m c_i \quad (7.4)
\]

We must distinguish between three cases:

1. The amount of solid is insufficient for producing a saturated solution \( (c_s < c) \)

\[
0 \leq \alpha \leq \alpha_x < 1 \quad (7.5)
\]

2. The amount of solid is exactly what can be dissolved in the solvent present \( (c_s = c) \)

\[
0 \leq \alpha \leq 1 \equiv \alpha_x \quad (7.6)
\]

3. There is an excess of solid \( (c_s > c) \)

\[
0 \leq \alpha \leq 1 < \alpha_x \quad (7.7)
\]

From (7.3) we derive

\[
\frac{dr}{dt} = \frac{\tau_0}{3 \alpha_x} \frac{d\alpha}{dt} \left( 1 - \alpha / \alpha_\infty \right)^{1/3} \quad (7.8)
\]

Inserting (7.1), (7.2), (7.4) and (7.8) into (2.6) we obtain

\[
\frac{d\alpha}{dt} = \frac{3DV_m c_s}{\tau_0^2} \left( 1 - \alpha / \alpha_\infty \right)^{1/3} \left( 1 - \alpha \right) \quad (7.9)
\]

If \( \alpha_x = 1 \) (i.e. case 2) (7.9) reduces to

\[
\frac{d\alpha}{dt} = \frac{3DV_m c_s}{\tau_0^2} \left( 1 - \alpha \right)^{1/3} \quad (7.10)
\]

with the solution

\[
k_d t = I_d (\alpha) \quad (7.11)
\]
where\[ k_d = 3DV_m c/r_s^2 = 4\pi Dr_n N \] (7.12)
\[ I_q(\alpha) = \int_{0}^{\infty} \frac{dx}{(1 - x)y^\frac{3}{2}} = 3\left[1 - \left(\frac{\alpha}{\alpha_\infty}\right)^{\frac{3}{2}} - 1 \right] \] (7.13)

If \( \alpha_\infty \neq 1 \) (cases 1 and 3) we define the new variable

\[ y = \frac{\alpha_\infty - \alpha}{\alpha_\infty - 1} \] (7.14)

and

\[ y_0 = \frac{\alpha_\infty}{\alpha_\infty - 1} \] (7.15)

If \( \alpha < \alpha_\infty \) (case 1) \( y_0 < y < 0 \). As time goes \( y \) increases from \( y_0 < 0 \) to 0, which value is reached at a certain finite time, see eq. (7.25). If \( \alpha > \alpha_\infty \) (case 3) \( 1 < y < y_0 \). In the course of time \( y \) decreases from \( y_0 > 1 \) to 1, which value is approached asymptotically, the half life periods converging, and equation (2.22) being valid for the limiting value, \( t \to t_0/2 \).

From (7.14) and (7.15) we derive\[ a = \alpha_\infty + (1 - \alpha_\infty) y \] (7.16)
\[ 1 - a = (1 - \alpha_\infty)(1 - y) \] (7.17)
\[ 1 - a/a_\infty = y/y_0 \] (7.18)
\[ da/dt = (1 - a) dy/dt \] (7.19)

Inserting (7.17), (7.18) and (7.19) into (7.9) we obtain

\[ \frac{dy}{dt} = \frac{3DV_m c_z}{r_0^2 y_0^{\frac{3}{2}}} y^{1/4}(1 - y) \] (7.20)

with the solution

\[ k_d t = I_D(x) = I_p(y) - I_D(y_0) \] (7.21)

where

\[ k_d = \frac{3DV_m c_z}{r_0^2 y_0^{\frac{3}{2}}} = \frac{k_d}{y_0^{1/3}} \] (7.22)

and where \( I_D \) is given by the same formula as in (2.13), although the integration interval is different. We may summarize that for a diffusion controlled growth or dissolution of a monodisperse suspension of spherical particles (and, approximately, other shapes of particles as well) in a closed system, the integrated rate equation is — except in one singular case — of the form

\[ kt = I_D(x) - I_D(x) \] (7.23)

where

\[ I_D(x) = \int_{0}^{x} x^{-\frac{3}{2}}(1 - x)^{-1} dx \] (7.24)

where \( x = \alpha \) (eq. (2.12) or (2.17)) for precipitation, and \( x = y \) (eq. (7.14)) for dissolution. The singular case is that in which the solid is just able to form a saturate solution with the solvent present. (Case 2, eqs. (7.11—13))
In dissolution experiments of the type, case 1 (excess solvent) the particles dissolve in a finite time, given by

$$t = \frac{I_D(y_o)}{k_s} = \frac{y_o^{1/2} I_D(y_o)}{4\pi DR_o N}$$  \hspace{1cm} (7.25)

Plots of $I_D(x)$ have been published earlier. A nomogram for obtaining numerical values is given in Figure 10. Theoretical progress curves for a closed system are shown in Figure 11.

![Figure 10. Nomogram for numerical values of the diffusion chronomal. Values between 0 and 1 correspond to growth, and values outside this interval correspond to dissolution experiments, as explained in the text.](image-url)
CONCLUSION

A couple of facts, viewpoints, methods and advices have been presented, that will hopefully assist students of precipitation and dissolution kinetics in finding out if their data may be explained (trivially?) only as effects of the transport processes, convection and diffusion, or if the data contain (valuable?) information about the molecular processes taking place in the surface of the growing or dissolving crystal. The discussion of these phenomena and their relative influence on the kinetics is also hoped to assist in planning experiments striving at collecting valuable data for the elucidation of the elementary steps, or for planning practical operations in pure science, industry or medicine.

REFERENCES

CRYSTAL GROWTH FROM SOLUTION

SAZETAK
Uvjetovanost rasta kristala iz otopina kontrolom transporta

A. E. Nielsen

Prikazom nekih činjenica, naziranja, metodologija istraživanja i savjetima onima koji istražuju rast ili otapanje kristala u vodenim otopinama, pokazuje se kako treba planirati eksperimente, tako da podaci ne budu samo odraz transportnih procesa, konvekcije i difuzije, već da sadržavaju i informacije o elementarnim molekulskim procesima na površini.

Kada neki kristal raste ili se otapa, njegov konstitucijski materijal mora prolaziti kroz difuzijsko polje. Za kristal koji miruje u otopini, brzina rasta ili otapanja određena je difuzijom kroz otopinu. Kristali mikrometarske veličine mogu se tijekom takvog eksperimenta smatrati stacionarnima. Za veće kristale konvekcija postaje faktorom koji određuje ukupnu brzinu procesa, te podaci dobiveni empirijskim kinetickim mjerenjima ne sadržavaju informacije o površinskim procesima. S obzirom na to da su za male kristale procesi transporta mnogo efikasniji, pokazano je kako se proučavanjem finih taloga mogu dobiti kvantitativni podaci o doprinosu pojedinih procesa u ukupnoj kinetičkoj brzini rasta ili otapanja kristala. Opće je pravilo da za proučavanje koeficijenata difuzije treba izabrati ekvivalent s malim kristalima i koncentracije u otopini koje su vrlo blizu ravnovesnoj topljivosti.

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