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# Rate Laws and Rate Constants in Crystal Growth*

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The mechanisms controlling the growth rate of electrolyte crystals precipitating from aqueous solution may be classified in eight types. Most of these are associated with a specific kinetics — linear, parabolic or exponential, — and composites of these kinetics are also found. A linear kinetics is found when the crystal grows by a rate controlled by the transport through the solution or the adsorption at unspecified positions at the crystal surface. Parabolic and exponential kinetics indicate that the growth rate is controlled by the integration at kinks with a rate determined by the cation dehydration frequency. The theory agrees satisfactorily with the empirical growth rates.

## MECHANISMS

When an electrolyte crystal grows from aqueous solution the following steps may be rate-determining[1-5]

1. Transport by convection in the solution
2. Transport by diffusion through the solution
3. Adsorption at the crystal/solution interface
4. Migration within the adsorption layer
5. Adsorption at a step (ledge) in the crystal surface
6. Migration along the step
7. Integration at a kink in a step
8. Partial or total dehydration of ions

### RATE LAWS I. ELEMENTARY RATE LAWS

A rate law is an equation of the form

$$\text{rate} = (\text{a constant}) \times (\text{a function of concentration(s)}) \tag{1}$$

A rate may be a flux ($j$) of matter (unit, $\text{mol/m}^2 \text{ s}$) or a linear velocity $v$ (unit, m/s). We shall prefer the latter type of rate. By $\dot{r}$ we mean the time derivative $dr/dt$; $r$ may be defined as the radius of a sphere with the same

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volume as the crystal — or otherwise. An elementary rate law is one which is determined by a single rate-determining step.

In the following we shall use $c$ = concentration of crystallizing solute, $c_s$ = solubility of crystal, $c - c_s$ = supersaturation, $S \equiv c/c_s$ = saturation ratio, $\sigma \equiv S - 1$ = relative supersaturation. We shall neglect activity coefficients. Corresponding to the mechanisms 1 to 8 we have the following elementary rate laws:

1. Convection: $\mathring{r} = k_C (S - 1) \equiv k_C \sigma$
2. Diffusion:  $\mathring{r} = k_D (S - 1) \equiv k_D \sigma$
3. Adsorption: $\mathring{r} = k_1 (S - 1) \equiv k_1 \sigma$
4. Two-dimensional diffusion: $\mathring{r}$ depends on the surface geometry
5. Adsorption at a step: $\mathring{r} = k' \times$ (step density) $(S - 1)$
6. One-dimensional diffusion: $\mathring{r}$ depends on step geometry
7. Integration:  $\mathring{r} = k'' \times$ (kink density) $(S - 1)$
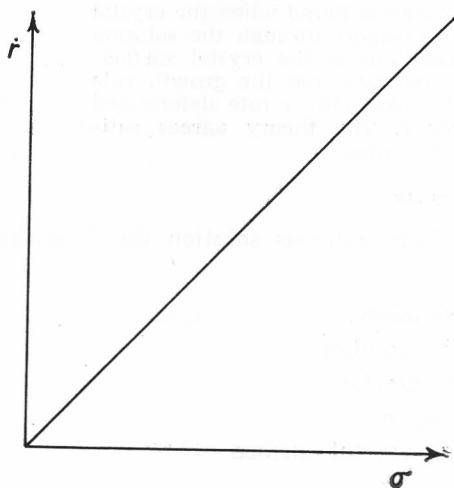8. Dehydration: $\mathring{r}$ depends on surface geometry



Figure 1. The linear rate law $\mathring{r} \sim \sigma$.

The *rate laws 1—3* are linear, of the general form

$$\mathring{r} = k_1 \sigma \tag{2}$$

see Figure 1. When a crystal grows by a surface spiral step (caused by a screw dislocation) the *step density* is proportional to ln $S$, and *rate law 5* becomes

$$\mathring{r} = k_2 (\ln S)(S - 1) \equiv k_2 [\ln (1 + \sigma)] \sigma \tag{3}$$

As $\ln S \equiv \ln (1 + \sigma) \approx \sigma$ for $|\sigma| \ll 1$ equation 3 may be substituted by

$$\mathring{r} = k_2 \sigma^2 \tag{4}$$

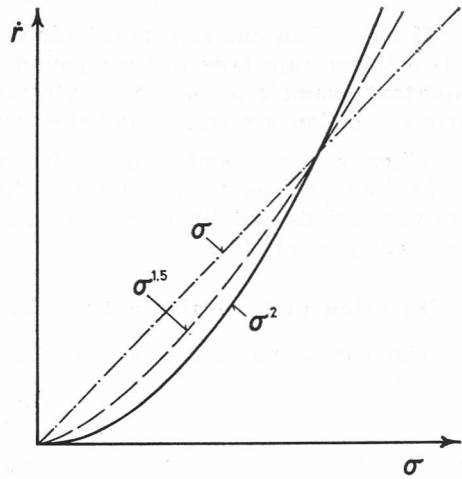at small supersaturations.[6] (Parabolic rate law; see Figure 2: $\sigma^2$).

Figure 2. The linear rate law $\dot{r} \sim \sigma$, the parabolic rate law $\dot{r} \sim \sigma^2$, and a quasiparabolic rate law $\dot{r} \sim \sigma^g$, shown for $g = 1.5$.

At spiral growth the kink density is proportional to $\ln S$ or $S^{1/2} \ln S$, depending on details of the assumptions (p. 45).[7] For $S \approx 1$ both expressions are equal to $S - 1$ $\sigma$, and rate law 7 (integration) becomes parabolic, of the same form as equation 4. Integration may also take place at kinks in steps which are the edges of surface nuclei. For that case the expression for the kink density is rather complex. A recent version of the rate law is[5]

$$\dot{r} = k_e \, S^{7/6} \, (S - 1)^{2/3}, \; (\ln S)^{1/6} \exp(-K_e/\ln S) \tag{5}$$

where $k_e$ and $K_e$ are constants. This is called an exponential rate low, and the curve $\dot{r}$ as a function of $\sigma$ has indeed a superficial resemblance with an exponential function, although, of course, $\dot{r} = 0$ for $\sigma = 0$. See Figure 3.
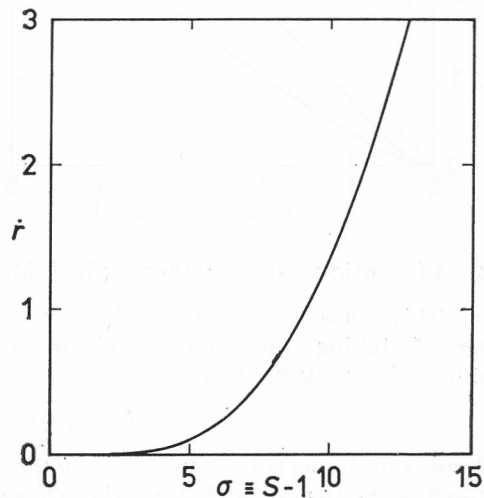
Figure 3. The exponential rate law, see equation 5.

### RATE LAWS II. COMPOUND RATE LAWS

If more than one step is rate-determining we have a compound rate law. If two linear rate laws are compounded the result is again a linear law. An important example of this is growth where convection, diffusion, and a linear surface reaction are controlling the rate (two of them, or all the three).

When a linear and a parabolic rate law are compounded because the mechanisms are consecutive, the resulting rate law will be parabolic for small supersaturations and linear for large supersaturations. There are two important examples of this.

### A. Diffusion and Parabolic Rate Law

The compound rate law may be written[3,5]

$$\sigma = \mathring{r}/k_1 + \sqrt{\mathring{r}/k_2} \tag{6}$$

or

$$\mathring{r} = \frac{2 k_1 k_2 \sigma^2}{2 k_2 \sigma + k_1 (1 + \sqrt{1 + 4 \sigma k_2/k_1})} \tag{7}$$

It is easy to see that for $\sigma \to 0$ $\mathring{r} \approx k_2 \sigma^2$; and for $\sigma \to \infty$ $\mathring{r} \approx k_1 \sigma$. See Figure 4: D+P.
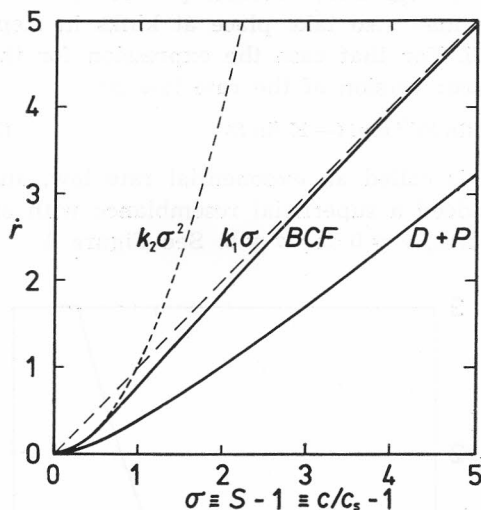


Figure 4. Compound rate laws: Diffusion and parabolic rate law, D + + P, see equation 7, and the hyperbolic tangent rate law, BCF, see equation 8.

### B. Adsorption and Surface Spiral Mechanism

This case was treated in the original Burton-Cabrera-Frank (BCF) paper,[6] taking the surface migration into account. The solution is the *hyperbolic tangent rate law.*

$$\mathring{r} = k_2 \sigma^2 \tan h (k_1/k_2 \sigma) \tag{8}$$

From the hyperbolic tangent function (see Figure 5) it follows that, for $\sigma \to 0$ $k_1/k_2 \sigma \to \infty$ and $\tan h (k_1/k_2 \sigma) \to 1$, $\mathring{r} \approx k_2 \sigma^2$; for $\sigma \to \infty$ $k_1/k_2 \sigma \to 0$,
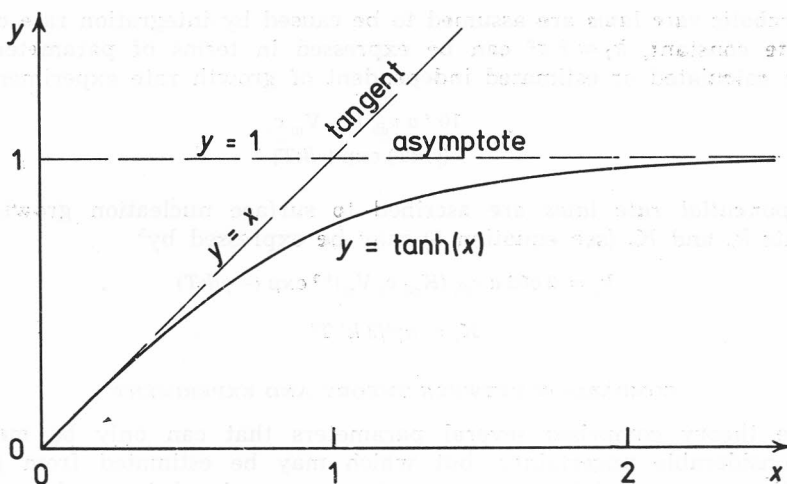
Figure 5. The hyperbolic tangent function (used in equation 8).

$\tan h \, (k_1/k_2 \, \sigma) \approx k_1/k_2 \, \sigma$, $\dot{r} \approx k_1 \, \sigma$. See BCF on Figure 4. We observe that the two ways of compounding $k_1 \, \sigma$ and $k_2 \, \sigma^2$ give widely different results.

In limited intervals of $\sigma$, any of the compound rate laws may be approximated by the »quasiparabolic« rate law,

$$\dot{r} = k_g \, \sigma^g \qquad (9)$$

which is generally used in engineering calculations.[3-11] (See Figure 1b: $\sigma^{1.5}$).

### RATE CONSTANTS I. TRANSPORT CONTROL

Pure *convection control* is only important under conditions of most violent stirring [ ref. 3, p. 290; ref. 12, p. 183]. For pure *diffusion control* [see ref. 7; 13, p. 209ff] of spherical particle growth[14]

$$k_1 = k_D = DV_m \, c_s/r \qquad (10)$$

and for compound *convection and diffusion* control[15]

$$k_1 = k_{CD} = DV_m \, c_s/\delta \qquad (11)$$

where, for a sphere[14,16] the diffusion layer thickness is

$$\delta = r/(1 + Pe^*)^{0.285} \qquad (12)$$

### RATE CONSTANTS II. SURFACE CONTROL

*Linear rate laws* are probably rate controlled by adsorption processes that need activation energy. The rate is typically $10^{-6}$ of the rate calculated for diffusion over the distance, $a =$ an atomic diameter $\approx 10^{-10}$ m [ref. 4, p. 266—8] or, in other words, the rate may be calculated by inserting an apparent diffusion layer thickness $\delta = 100 \, \mu m$ in equation 11 [ref. 5, Table 6]. With $D \approx 10^{-9}$ m²/s these statements correspond to

$$k_1 \equiv \dot{r}/\sigma = DV_m \, c_s/\delta = (10^{-5} \text{ m/s}) \, V_m \, c_s \qquad (13)$$

*Parabolic rate laws* are assumed to be caused by integration rate control. The rate constant, $k_2 \equiv \hat{r}/\sigma^2$ can be expressed in terms of parameters that may be calculated or estimated independent of growth rate experiments[5,17,18]

$$k_2 = \frac{10^{-4} a \, \nu_{dh} \, K_{ad} \, V_m \, c_s}{(\gamma/kT) \exp(\gamma/kT)} \tag{14}$$

*Exponential rate laws* are ascribed to surface nucleation growth. The constants $k_e$ and $K_e$ (see equation 5) may be expressed by[5]

$$k_e = 0.002 \, a \, \nu_{dh} \, (K_{ad} \, c_s \, V_m)^{4/3} \exp(-\gamma/kT) \tag{15}$$

$$K_e = \pi \gamma^2/3 \, k^2 \, T^2 \tag{16}$$

## COMPARISON BETWEEN THEORY AND EXPERIMENT

The theory comprises several parameters that can only be measured with considerable uncertainty, but which may be estimated from general correlations, supported by measurements on several substances ($\gamma$ and $K_{ad}$). The best way to compare theoretical and experimental crystal growth rates may therefore be to use a generalized rate diagram such as Figure 6, where the theoretical rates are plotted (as isograms) as a function of generally accepted experimental parameters ($c_s$ and $\nu_{dh}$).

In Figure 6 the vertical and sloping lines marked with values of log ($k$/pm s$^{-1}$) indicate the theoretical values of $k$ for linear rate law (vertical lines, see equation 13) and parabolic rate law (sloping lines, see equation 14).

For electrolytes where the growth rates have been measured we have plotted the following:

(1) A black point symbol (circular for linear and square for parabolic rate law) at ($c_s$, $\nu_{dh}$).

(2) A small bar (connected to the corresponding point mentioned under (1)) indicating the experical rate constant.

The length of the line connecting the point symbol and the bar indicating the value of $k$ is equal to the deviation between the theoretical and experimental value of the growth rate.

## CONCLUSIONS

From figure 6 we observe that the experimental and theoretical values in general deviate less than or about one decade from each other. Taking into regard that the total range of values is about eight decades (3 to 2 × 10$^8$ pm/s) the results may be taken as a confirmation of the general features of the theory. It is particulary satisfactory that the electrolytes with many (6—7) water molecules of crystallization do not agree with the assumption that the rates are determined by the dehydration of the cations, but rather grow by the maximal rate allowed by diffusion. This alternative explanation is modelled by letting $\nu_{dh} = 10^9$ s$^{-1}$, see the *small* circular point symbols a, b and c at log ($\nu_{dh}$/s$^{-1}$) = 9.
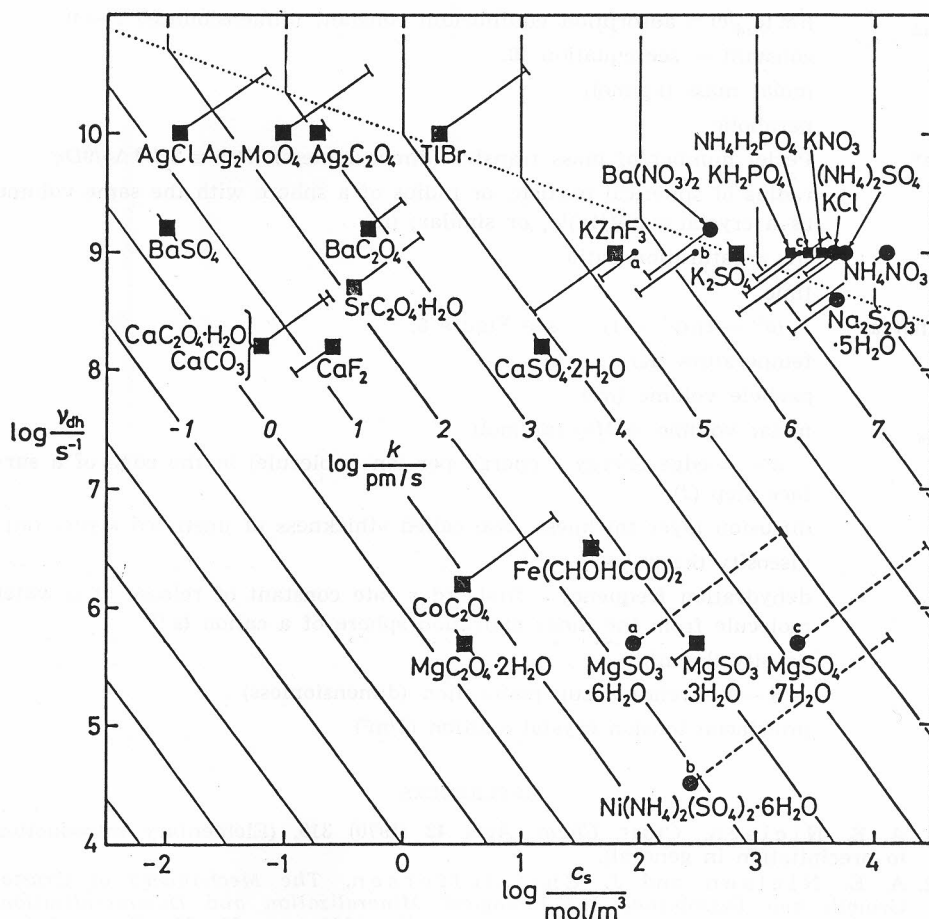
Figure 6. Generalized crystal growth rate diagram. Points in the diagram correspond to the coordinates, solubility ($c_s$) and cation dehydration frequency ($\nu_{dh}$). The vertical and sloping lines marked with log (growth rate constant) $= -1, 0, \ldots 7$ are isograms according to the theory. Black points: ($c_s$, $\nu_{dh}$) for electrolyte crystals investigated; small bars connected to the black points: Experimental values of log (rate constant) on the same scale as the theoretical isograms.

GLOSSARY OF SYMBOLS, WITH SI UNITS

| | |
|---|---|
| $a$ | ionic or molecular diameter ($\approx 10^{-10}$ m) |
| $c$ | concentration (mol/m³); $c_s$ solubility; $c_{ad}$ concentration in adsorption layer (of thickness, $a$) |
| $C$ | convection; $CD$ convection and diffusion |
| $D$ | diffusion; diffusion coefficient ($\approx 10^{-9}$ m²/s) |
| $g$ | growth rate index (normally $1 \leq g \leq 2$) |
| $G$ | acceleration of gravity (9.81 m/s²) or gravity + acceleration |
| $k$ | Boltzmann constant ($1.38 \times 10^{-23}$ J K⁻¹); $k_1$ linear rate constant (m/s); $k_2$ parabolic rate constant (m/s); $k_e$ — see equation 15. |

$K_{ad}$        $\lim (c_{ad}/c)$ = adsorption equilibrium constant (dimensionless) $c \rightarrow 0$

$K_e$         constant — see equation 16.

$M$          molar mass (kg/mol)

$P$          parabolic

$Pe^*$        Peclet number of mass transfer (dimensionless); $Pe^* \equiv 2Gr^3 \Delta\varrho/9D\eta$

$r$          radius of spherical particle, or radius of a sphere with the same volume
             as a crystal $= (3V/4\pi)^{1/3}$, or similar; (m)

$S$          $c/c_s$ = saturation ratio

$t$          time

$\tan h\,(x)$    $\equiv (e^{2x} - 1)/(e^{2x} + 1)$ — see Figure 5.

$T$          temperature (K)

$V$          particle volume (m³)

$V_m$         molar volume $\equiv M/\varrho$ (m³/mol)

$\gamma$          $= a^2\sigma_\gamma$ = edge energy = energy per ion (molecule) in the edge of a sur-
             face step (J)

$\delta$          diffusion layer thickness, also called »thickness of unstirred layer« (m)

$\eta$          viscosity (kg m⁻¹ s⁻¹)

$\nu_{dh}$         dehydration frequency = first-order rate constant of release of a water
             molecule from the inner hydration sphere of a cation (s⁻¹)

$\varrho$          density (kg/m³)

$\sigma$          $\equiv S - 1 \equiv$ relative supersaturation (dimensionless)

$\sigma_\gamma$         interfacial tension crystal/solution (J/m²)

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## SAŽETAK

### Kinetički zakoni i konstante u rastu kristala

#### A. E. Nielsen

Mehanizmi kontrole brzine rasta kristala elektrolita koji se talože iz vodenih otopina mogu se razvrstati u osam tipova. Većina ih je povezana sa specifičnom kinetikom — linearnom, parabolnom ili eksponencijalnom — ali su također nađeni i međuslučajevi. Linearna kinetička funkcija nađena je u slučaju kad je brzina rasta kristala kontrolirana transportom materijala kroz otopinu ili adsorpcijom na nespecificiranim mjestima na kristalnoj površini. Parabolna i eksponencijalna kinetička funkcija pokazuju da je brzina rasta kontrolirana ugrađivanjem na prijevojima brzinom određenom učestalošću hidratizacije kationa. Teorija se zadovoljavajuće slaže s empirijskim brzinama rasta.