

## The Kinetics of Crystal Growth in Barium Sulfate Precipitation

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The kinetics of barium sulfate precipitation is followed turbidimetrically and conductometrically. It is found that when the concentration of  $\text{Ba}^{++}$  and  $\text{SO}_4^-$  are larger than about 0.4 mM the kinetics may be expressed by

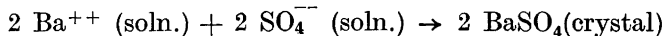
$$k_D t = \int_0^a \alpha^{-1/3} (1 - \alpha)^{-1} d\alpha$$

where  $t$  is the time and  $a$  the degree of reaction (precipitation). When the said concentrations are smaller than 0.4 mM, approximately, the kinetics observed agrees with

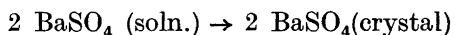
$$k_R t = \int_0^a \alpha^{-2/3} (1 - \alpha)^{-4} d\alpha$$

These findings agree with the assumption that below 0.4 mM the rate determining step in the crystal growth process is a fourth order reaction at the crystal-solution interface and, above 0.4 mM, the diffusional transport of matter from the bulk of the liquid to the surface of the growing crystals.

In a previous work on the kinetics of electrolyte precipitation<sup>1</sup> it was concluded that the rate of growth of barium sulfate crystals is controlled by some sort of chemical reaction with the rate determining step



or, perhaps



taking place in the surface of the growing particles. This was found to be in agreement with experiments where the concentration of barium sulfate was less than 0.2 mM. In this work the experimental range is extended to much higher concentrations and it is observed that the above mentioned mechanism ceases to be rate determining at higher concentrations. According to the fourth order law the rate of crystal growth increases with the fourth power of concentration. Above 0.4 mM the rate becomes too high for the matter to diffuse

sufficiently fast to the surface of the crystals and therefore diffusion becomes the bottle-neck of the growth process. Nernst<sup>2</sup> and Brunner<sup>3</sup> found the dissolution process for several salts to be diffusion controlled, but the kinetics of the reverse process turned out<sup>4</sup> to be more difficult to explain.

It has been shown<sup>1</sup> that when the growth of a constant number of small particles of the same size is diffusion controlled, the degree of reaction  $\alpha$  depends on time according to

$$k_D t = \int_0^{\alpha} \alpha^{-1/3} (1 - \alpha)^{-1} d\alpha = I_D$$

and when the rate is controlled by a fourth order reaction in the surface

$$k_R t = \int_0^{\alpha} \alpha^{-2/3} (1 - \alpha)^{-4} d\alpha = I_4$$

From this follows that if  $I_D$  is plotted against time a straight-line plot is obtained if the rate is determined by diffusion. In the following we shall prefer to plot  $\log I_D$  against  $\log t$ . This should give parallel straight lines 45° to the axis.

#### EXPERIMENTAL

The reacting systems were supersaturated solutions of  $\text{BaSO}_4$  prepared by mixing equal volumes of solutions of the same molarity ( $2c_0$ ) of  $\text{BaCl}_2$  and  $\text{Na}_2\text{SO}_4$ . In three experiments  $\text{NaCl}$  was added in order to get the required ionic strength.

The advancement of the reaction was measured in two different ways: in the fastest experiments ( $c_0 \geq 1$  mM) the electric conductivity was measured with Radiometer's direct reading AC(70-3 000 c/s) conductivity meter. The degree of reaction  $\alpha$  was found from the conductivity by means of a chart based on measurements of the conductivities of mixtures of solutions of  $\text{BaCl}_2$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$ . The slower experiments were followed photometrically by means of an apparatus especially designed by Dr. J. Koefoed (of this institute) for measuring small optical densities. The voltages from the measuring selenium photocell and a similar reference cell both illuminated from the same lamp were compensated one against the other, giving the light intensity ratio  $I_0/I$  as the ratio of the resistors of the compensating bridge. From  $I_0/I$   $\alpha$  was found by taking  $(\log(I_0/I))^{3/2}$  proportional to  $\alpha$ . In order to find the proportionality factor the electric conductivity was measured at the end of each experiment. The advantage of not following the whole experiment conductometrically consists in that it is not necessary, then, to remove the layer of barium sulfate formed on the walls of the conductivity cell.

It is well known<sup>5</sup> that under these conditions the barium sulfate precipitation is a rather irreproducible process. The reason for this is probably that the number of particles formed per unit of volume comes out very differently even if one tries to make several identical experiments consecutively<sup>6</sup>. But during a precipitation experiment the number is constant and from microscopy it seems that the shape of the particles does not change much during growth. Therefore it is reasonable to put the volume proportional to the three halves power of the surface of the precipitate and this, again, proportional to the logarithm of the light intensity ratio  $I_0/I$ . Table 1 shows how the calculations were made.

In experiments with added salt (for ionic strength) it would be a rather inexact method to find  $\alpha$  from electric conductivity. Instead of this  $\alpha$  was found by putting it equal to  $1/7 = 0.143$  (as is required by the formula for  $I_4$ ) at the point of inflexion on the curve of  $(\log(I_0/I))^{3/2}$  against  $t$ . Since the point of inflexion in case of  $I_D$  is at  $\alpha = 1/4 = 0.25$  this method can only be applied when it is known that the experiments follow  $I_4$ . This assumption is confirmed through the rectilinear arrangement of the points (squares and triangles) on Fig. 3.

The temperature was always between 22 and 23°C. All conductivities were corrected to 22.0°C by means of the empirically determined temperature coefficient  $d\kappa/dt = 0.022 \kappa$ .

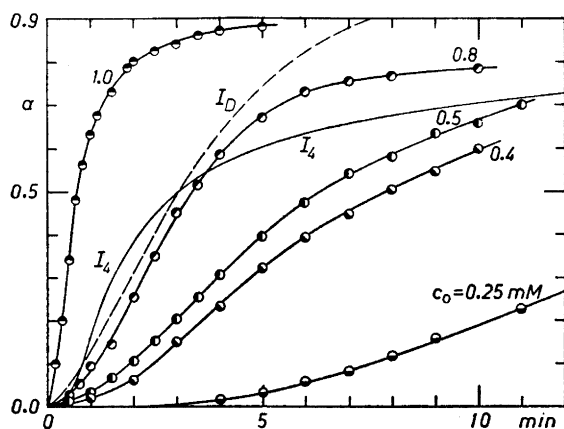


Fig. 1. The fraction  $\alpha$  of the  $\text{BaSO}_4$  present having deposited on the crystals at time  $t$ .  $I_D$  and  $I_4$  are theoretical curves (in arbitrary time units) corresponding to diffusional and fourth-order-surface-reaction rate control, respectively. The experimental curves resemble  $I_D$  at small  $t$  (high concentration) and  $I_4$  at large  $t$  (low concentration) as required by theory.

## RESULTS

In Fig. 1 are some of the experimental values of  $\alpha$  plotted against the time. For comparison  $I_D$  and  $I_4$  — from numerical integration — are also shown, in arbitrary time units. It is seen that the experimental curves, except those of the lowest  $c_0$ , have the shape of  $I_D$  at small times (high concentrations) and become more like  $I_4$  in the later parts of the experiments.

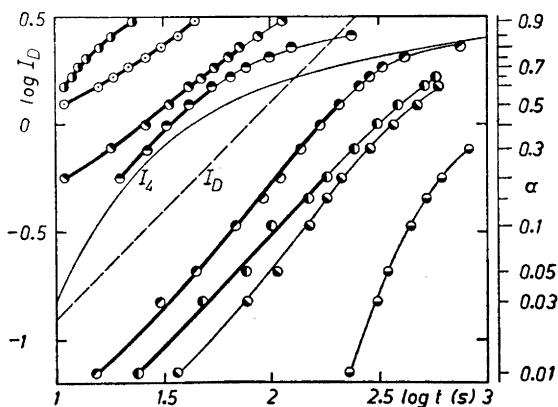


Fig. 2. A transformation of Fig. 1, which yields straight lines in case of diffusional rate control. The heavy (parts of the) lines correspond to  $(\text{BaSO}_4) > 0.4 \text{ mM}$ .

Table 1. 50 ml 1.6 mM BaCl<sub>2</sub> + 50 ml 1.6 mM Na<sub>2</sub>SO<sub>4</sub>; c<sub>0</sub> = 0.8 mM.

<i>t</i> min	<i>I</i> <sub>0</sub> / <i>I</i>	<i>a</i>	<i>l</i> μ	$\Delta l$ μ	$\Delta l/\Delta t$ μ/min	mμ/s	<i>c</i> mM
0.5	1.013	0.025	1.67				
1.0	1.032	0.094	2.60	1.33	1.33	21.2	0.725
1.5	1.045	0.144	3.00				
2.0	1.063	0.253	3.60	1.02	1.02	17.0	0.598
2.5	1.079	0.350	4.02				
3.0	1.094	0.450	4.38	0.56	0.56	9.3	0.440
3.5	1.103	0.514	4.58				
4.0	1.112	0.582	4.76	0.62	0.31	5.2	0.334
5.0	1.124	0.670	5.00	0.38	0.19	3.15	0.264
6.0	1.132	0.730	5.14	0.20	0.10	1.67	0.216
7.0	1.135	0.755	5.20	0.09	0.045	0.75	0.196
8.0	1.137	0.768	5.23				
10.0	(1.139)	(0.785)	5.26				

Comments on Table 1. Immediately after the measurements at  $t = 10$  min the solution was stirred and a drop transferred to a blood cell counting chamber of volume 0.9 mm<sup>3</sup>, and 202 particles were counted;  $N = 202/0.9 = 224$  mm<sup>-3</sup>. From this number and  $c_0 = 800$  μM  $l_\infty$  was found by means of

$$l_\infty = \sqrt[3]{800 \times 52/224} = 5.71 \mu$$

The value of  $I_0/I$  at  $t = 10$  min (1.139) is extrapolated, since at this moment the electric conductivity was measured:  $\kappa = 224 \times 10^{-6}$  ohm<sup>-1</sup> cm<sup>-1</sup> (uncorrected) at 22.3°C. This corresponds to  $\kappa = 222.5 \times 10^{-6}$  ohm<sup>-1</sup> cm<sup>-1</sup> at 22.0°C. Applying a chart based on empirical values of  $\kappa$ ,  $a$  was found to be 0.785 at  $t = 10$  min. The other values of  $a$  were calculated by means of

$$a = 0.785 [\log(I_0/I)/\log 1.139]^{1/2}$$

and  $l$  was obtained from

$$l = l_\infty a^{1/2}$$

In this and similar experiments  $\Delta l/\Delta t$  was found directly from the measured values using intervals symmetric about the experimental  $t$ -values. This gives a reasonable degree of smoothing and reduces the calculating work. (In the fastest experiments all  $a$ -values were found conductometrically and had to be smoothed graphically before the differentiation).

Finally  $c$  was found as  $(1-a)c_0$ .

In Fig. 2  $\log I_D$  is shown as a function of  $\log t$ . The part of the curves where (BaSO<sub>4</sub>) < 0.4 mM is drawn in a heavier line than the rest of the curves. The high-concentration-parts of the curves are more straight than the low-concentration-parts.

Fig. 3 displays the dependence of the linear growth rate  $dl/dt$  on time;  $l$  is the length of the edge in a cube of the same volume as the single crystals. The growth rate was obtained from the measurements in the following way. The value of  $l$  at "infinite time"  $l_\infty$  was calculated from the molar volume of barium sulfate, 52 cm<sup>3</sup>/mole, the concentration  $c_0$  of barium sulfate at  $t = 0$  in the unit μM and the number  $N$  of particles per mm<sup>3</sup>, by means of

$$l_\infty = (52c_0/N)^{1/3} \quad (\text{microns})$$

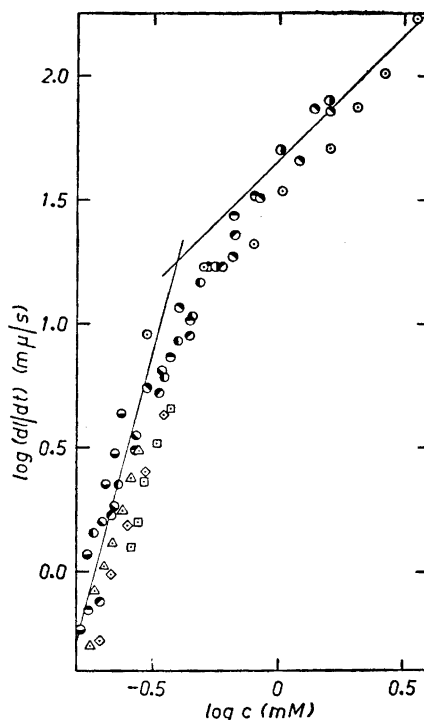


Fig. 3. The linear rate of crystal growth as function of ( $\text{BaSO}_4$ ) in a logarithmic diagram. Below 0.4 mM ( $\log c = -0.4$ ) the rate increases proportional to the fourth power of concentration, above 0.4 mM the rate is directly proportional to the concentration of the supersaturated barium sulfate solution. The asymptotes are drawn without regard to the triangular and square "points".

$l$  was found by multiplying  $l_\infty$  with  $\alpha^{1/3}$ . Then  $dl/dt$  could be obtained through numerical differentiation. In a few cases (of very high  $c_0$ ) the  $\alpha$ -values had to be smoothed by means of a graph like Fig. 1.

The straight lines drawn in Fig. 3 are the apparent asymptotes to the curve determined by the points. Their inclinations are 4 and 1 respectively, and from the figure their equations are seen to be, respectively

$$\begin{aligned} \log(dl/dt) &= 4 \log c + 2.80 && (c < 0.3 \text{ mM}) \\ \log(dl/dt) &= \log c + 1.65 && (c > 0.6 \text{ mM}) \end{aligned}$$

which is equivalent to

$$\begin{aligned} dl/dt &= 630 c^4 && (c < 0.3 \text{ mM}) \\ dl/dt &= 45 c && (c > 0.6 \text{ mM}) \end{aligned}$$

when  $dl/dt$  is measured in  $m\mu/s$  and  $c$  in mM.

Similar points, even in different figures, refer to the same run of a kinetic experiment.

#### Salt effect

A reaction between two  $\text{Ba}^{++}$ - and two  $\text{SO}_4^{--}$ -ions must be subject to a large negative kinetic salt effect, decreasing the growth rate at higher ionic strengths, although it would probably be misleading to try to calculate it

from the Debye-Hückel limiting law or similar generalized expressions for the activity coefficients. Since this salt effect will reduce the rate most at high concentrations just as diffusion, it is important to know its magnitude. At the highest concentrations investigated ( $c_0 = 5$  mM, circular "points" with a dot in the centre) the ionic strength was 0.030 M. In the experiments shown by square and triangular "points" with a dot in the centre the ionic strength was therefore adjusted to 0.030 M by means of NaCl. In this way all points with a dot in the centre correspond to experiments with approximately the same ionic strength. As expected there is a negative salt effect, since the "dotted" points mostly lie about 0.3 decadic units below the other points, showing that the addition of salt has halved the rate of crystal growth. This effect is, however, by far too small to explain the deviation from the fourth-power-law.

#### The rate of diffusion

On the other hand we may calculate from the diffusion coefficient of barium sulfate the greatest possible rate of transport of matter from the bulk of the solution to the surface of the growing particles. The geometry of the diffusional area looks rather different in case of a large and a small particle. For large particles Nernst<sup>2</sup> pointed out that the phenomenon may be described by means of a diffusion layer of thickness 10–100  $\mu$ , depending, among other things, on the stirring rate. But for particles of radius  $r$  comparable with or smaller than the thickness of such a diffusion layer Smoluchowski<sup>7</sup> showed by means of Fick's diffusion laws, that after a very short time (a fraction of a second) the concentration around such a "spherical sink" follows

$$(dc/dx)_{x=r} = (c - c_r)/r$$

where  $x$  is the distance from the center of the sink. In the present case we may neglect  $c_r$  in  $c - c_r$ . In the experiments on barium sulfate reported here  $c_r$  is about  $c/100$ . We then have, by Fick's first law, for the amount of matter deposited in unit time

$$dn/dt = 4\pi r^2 D (dc/dx) = 4\pi r c D$$

If this is multiplied by the molar volume of  $\text{BaSO}_4$  one gets the rate, by which the volume increases

$$v \times 4\pi r c D = v dn/dt = d(\frac{4}{3}\pi r^3)/dt = 4\pi r^2 dr/dt$$

or

$$dr/dt = v D c / r$$

Now we may use this in an estimate even though the actual particles are not spherical. In the following it will be convenient to express the volume of the crystals by means of the length  $l$  of the edge in a cube of the same volume, and we may substitute

$$l^3 = \frac{4}{3}\pi r^3 = 4.19r^3; l = 1.61r; l^2 = 2.60r^2$$

so that  $dl/dt = 2.60vDc/l$ . The diffusion coefficient of  $\text{BaSO}_4$  may be calculated from the electric mobilities according to Nernst<sup>8</sup>

$$D = 2D_+D_-(D_+ + D_-)$$

where

$$D_+ = kTl_+/q_+$$

$$D_- = kTl_-/q_-$$

Here  $l_+$  and  $l_-$  are the electric mobilities of the  $\text{Ba}^{++}$  and  $\text{SO}_4^{--}$  ions, respectively, and  $q_+ = q_- = q$  the electric charges of the ions, that is twice the proton charge. When we insert<sup>9</sup>  $l_+ = 6.59 \times 10^{-4}$ ,  $l_- = 8.27 \times 10^{-4}$   $\text{cm}^2/\text{s}\cdot\text{V}$  and  $2kT/q = 0.02569\text{V}$  we find the diffusion coefficient of barium sulfate

$$D = (2kT/q)l_+l_-/(l_+ + l_-) = 9.42 \times 10^{-6} \text{ cm}^2/\text{s} \text{ (at } 25^\circ\text{C)}$$

Since the molar volume is  $M/d = 233.4/4.499 = 51.9 \text{ cm}^3/\text{mole}$  (at  $15^\circ\text{C}$ ) we have

$$dl/dt = 2.60vDc/l = 1.27 \times 10^{-3}c/l$$

where  $dl/dt$  is measured in  $\text{cm}/\text{s}$ ,  $c$  in  $\text{mole}/\text{cm}^3$  and  $l$  in  $\text{cm}$ ; if we change to  $\text{m}\mu/\text{s}$ ,  $\text{mM}$  and  $\mu$ , respectively, we get

$$dl/dt = 127c/l$$

From Fig. 3 we have from the upper asymptote

$$dl/dt = 45c$$

Now these two formulae cannot be compared directly since  $l$  is a parameter in only one of them. But we may substitute for  $l$  the mean value of all the experimental points, (half-black—half-white) closest to the upper line in Fig. 3. We have from the experiments the following values of  $l$ : 2.67, 3.39, 3.93, 4.34, 3.00, 4.96, 1.62 and 1.93  $\mu$ . The arithmetic mean value is 3.23  $\mu$ . This gives

$$dl/dt = 127c/3.23 = 39c$$

The experimental value of the coefficient (45) and the value calculated from the diffusion theory (39) agree within the accuracy of the measurements.

In Fig. 3 the two asymptotes intercept at  $\log c = -0.4$ , that is  $c = 0.4 \text{ mM}$ . We may therefore say that the rate determining mechanism of crystal growth of barium sulfate changes from a fourth order surface reaction into diffusion around  $c = 0.4 \text{ mM}$ . Further evidence of this is obtained by microscopy. The precipitate formed when  $c_0 < 0.5 \text{ mM}$  consist of small prisms, which in the microscope look like rectangles with the longer side approximately twice as long as the shorter one. With initial concentrations between 0.5 and 1.5  $\text{mM}$  the particles are more or less distorted prisms, the corners having grown more than the middle of the faces. And at  $c_0 > 1.5 \text{ mM}$  the corners have grown far more than the other parts of the crystals, giving them the appearance of "stars"; see Figs. 2 and 3 in the previous work<sup>6</sup>. This appearance is to be expected in case of diffusional control of the growth rate, since the concentration then is greatest at the corners. The rectangular (orthorhombic)

shape is obtained when the concentration is approximately the same all over the surface, and it cannot be so when the consumption of matter is fast compared with the diffusion.

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Received February 18, 1958.