

The Kinetics of Crystal Growth in Barium Sulfate Precipitation

III. Mixed Surface Reaction and Diffusion Controlled Rate of Growth

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The chronometric integrals for precipitation processes where the crystal growth velocity is controlled simultaneously by fourth-order surface reaction and diffusion are calculated numerically and found to agree with the experiments.

The method reported constitutes a new experimental method for obtaining rate-constants and diffusion coefficients.

In a previous article¹ the chronometric integrals for the pure cases of diffusion or p -th order surface reaction rate control of crystal growth in precipitation processes were expressed in terms of known functions and tabulated (for $p = 1, 2, 3$ and 4), and the general differential equation between the degree of advancement α and time t was derived also for the case where both types of rate control were effective at once. This equation has previously² been solved in terms of known functions for $p = 1$ only.

In the following we restrict the treatment to cases where the solubility of the substance is so small that it can be neglected ($s/c_0 < 0.05$). The crystals are assumed spherical. Only in cases of very flat or long crystals this will give errors larger than 10–20 %. We may write the solution to the "pure cases" thus

1. Diffusional rate control:

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

2. p -th order surface reaction:

$$t = K_p \int_0^\alpha \frac{d\alpha}{\alpha^{2/3}(1-\alpha)^p} = K_p I_p(\alpha)$$

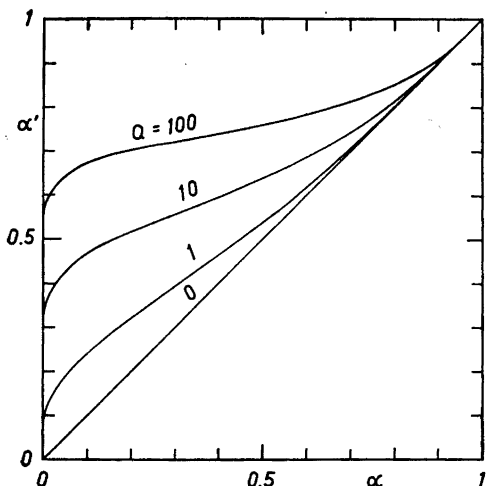


Fig. 1. The relation between the "effective" degree of advancement at the crystal surface α' , and α , for different values of Q . The difference between α and α' is caused by the slowdown of the reaction by diffusion. Q is a measure of this influence; Q is a constant during the reaction.

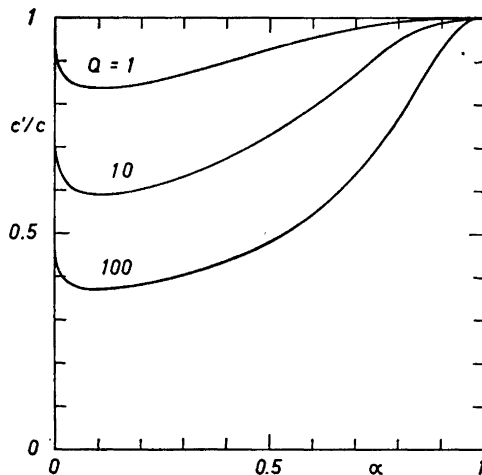


Fig. 2. The ratio between the concentration at the surface and in the bulk solution, when both diffusion and fourth-order surface reaction are rate determining.

where $K_D = r_1^2/3vDc_0$, $K_p = r_1/3vk_p c_0^p$, r_1 = particle radius when $\alpha = 1$, v = molar volume of precipitate, D = diffusion coefficient, c_0 = concentration when $t = 0$ (and $\alpha = 0$), k_p = p -th order surface reaction rate constant.

For $p = 1$ the solution to the "mixed case" is simply ²

$$t = K_D I_D(\alpha) + K_1 I_1(\alpha)$$

For $p > 1$ the solution has not been found explicitly. In order to get a numerical solution we use the equation derived in the previous paper ¹

$$\frac{dr}{dt} = \frac{vD(c-c')}{r} = vk_p(c')^p$$

where c' is the concentration at the surface of the crystal. We define α' by $c' = c_0(1-\alpha')$ and derive

$$\alpha' - \alpha = (K_D/K_p)(1-\alpha')^p \alpha^{1/3}$$

The dimensionless quantity $Q \equiv K_D/K_p = r_1 k_p c_0^{p-1}/D$ is constant during each single experiment (when the number of crystals is constant and they are all alike), and if we solve, for fixed p and Q , the equation

$$\alpha' - \alpha = Q(1-\alpha')^p \alpha^{1/3}$$

with respect to α' for a series of values of α , (see Figs. 1 and 2), we can calculate the following integrals

$$t = K_D \int_0^\alpha \frac{d\alpha}{\alpha^{1/3}(\alpha' - \alpha)} = K_p \int_0^\alpha \frac{d\alpha}{\alpha^{2/3}(1 - \alpha')^p}$$

$$= K_D I_{DpQ}(\alpha) = K_p I_{pDQ}(\alpha)$$

The result of this procedure is given in Table 1 for $p = 4$ and for several values of Q . Since

$$I_{pDQ}/I_{DpQ} = K_D/K_p = Q = \text{a constant}$$

it is not necessary to tabulate both the integrals.

In order to compare experimental results with these integrals it is probably best to plot α as a function of $\log t$ on transparent paper and slide this over a plot of α as a function of $\log I_{pDQ}$ or I_{DpQ} (see Fig. 3).

If the kinetics is of the kind discussed here, one may find Q and for instance the value $t_{0.5}$ of t for $\alpha = 0.5$. This has been done for experiments on BaSO_4^1 and from the results Fig. 4 was drawn, to show a typical example of how Q varies with c_0 .

In case of very exact measurements it may be necessary to use Q -values corresponding to curves not given in Fig. 3. For this purpose another method is suggested. The shape of the experimental curve may be expressed by the ratio

$$\Theta = t_{0.75}/t_{0.25}$$

From Fig. 5 the corresponding Q is found.

Table 1. The precipitation chronomals I_{4DQ} .

$Q =$ α	0.1	0.2	0.5	1	2	5	10	20	50	100
0.001	0.30	0.31	0.33	0.36	0.40	0.54	0.73	1.07	1.95	3.32
0.01	0.69	0.71	0.79	0.91	1.10	1.60	2.46	3.81	7.59	13.3
0.05	1.27	1.35	1.57	1.90	2.46	3.90	6.12	9.88	20.3	36.2
0.10	1.72	1.84	2.19	2.70	3.59	5.87	9.29	15.25	31.7	57.0
0.15	2.10	2.26	2.72	3.40	4.57	7.58	12.07	20.0	41.7	75.1
0.20	2.49	2.70	3.26	4.09	5.54	9.27	14.8	24.6	51.4	92.7
0.25	2.90	3.14	3.82	4.81	6.69	10.94	17.5	29.1	61.0	109.9
0.30	3.37	3.65	4.44	5.59	7.59	12.6	20.4	33.9	70.9	128
0.35	3.92	4.23	5.14	6.46	8.75	14.6	23.4	38.8	81.0	146
0.40	4.60	4.96	5.98	7.48	10.09	16.8	26.7	44.3	91.9	165
0.45	5.46	5.86	7.02	8.70	11.65	19.2	30.4	50.2	103.7	186
0.50	6.60	7.05	8.34	10.23	13.5	22.1	34.6	56.9	117.0	209
0.55	8.18	8.67	10.12	12.21	15.9	25.5	39.6	64.6	132	234
0.60	10.45	11.02	12.6	15.0	19.1	30.0	46.0	74.3	150	264
0.65	14.0	14.6	16.4	19.0	23.6	36.0	54.1	86.0	170	298
0.70	20.1	20.8	22.7	25.7	30.9	45.2	65.9	102.3	198	343
0.75	31.5	32.1	34.2	37.5	43.5	60.0	83.6	125.4	236	401
0.80	55.0	56.4	58.9	62.3	69.2	88.6	116.5	166	295	489
0.82	72.8	73.3	75.3	79.4	86.5	107.2	138	193	331	539
0.84	100.0	100.5	102.3	105.9	114.8	137	171	232	380	604
0.86	145	146	148	152	160	183	221	284	450	696
0.88	223	224	226	230	239	264	305	380	561	829
0.90	376	377	378	384	394	422	464	543	749	1053
0.92	716	718	721	724	736	767	818	912	1131	1400

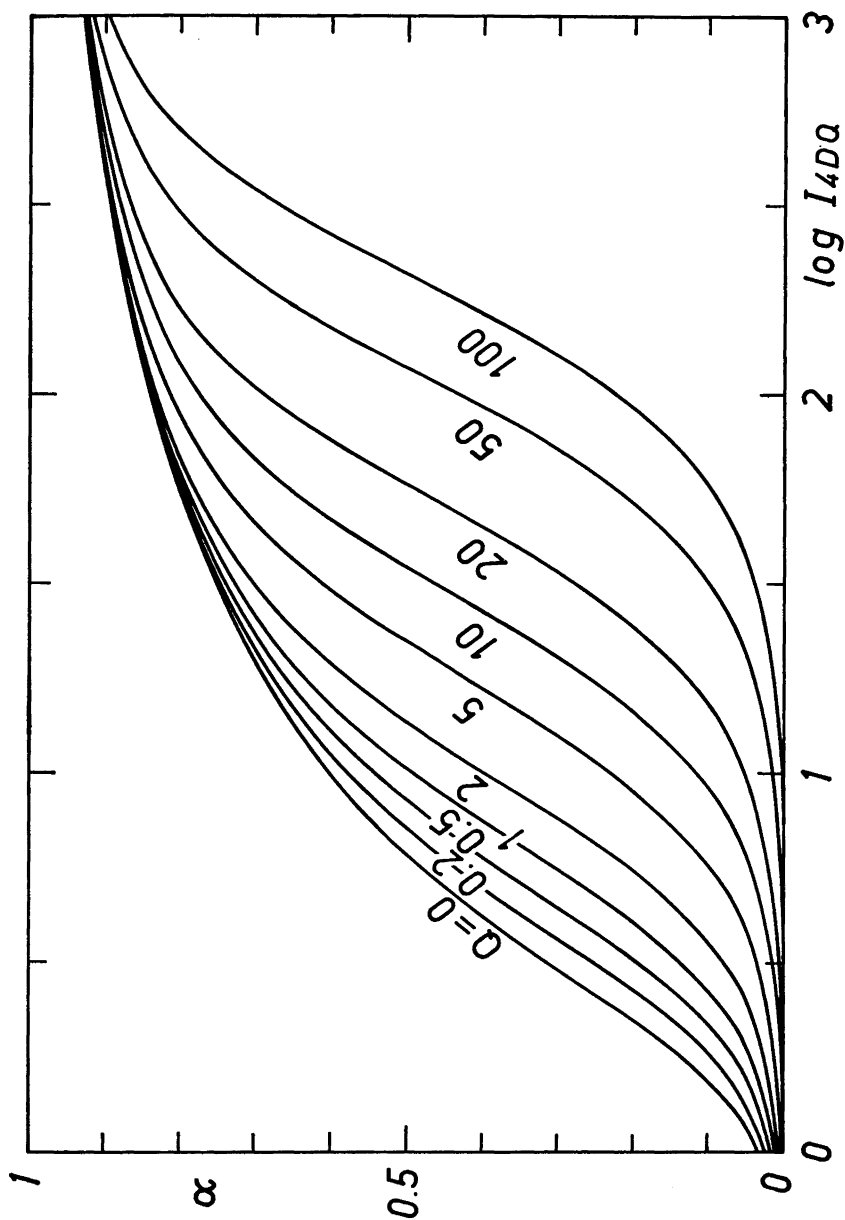


Fig. 3. A semi-logarithmic plot of α versus the chromonals I_4DQ . For check of kinetics and determination of Q ; plot α versus $\log t$ on transparent paper and slide over this figure.

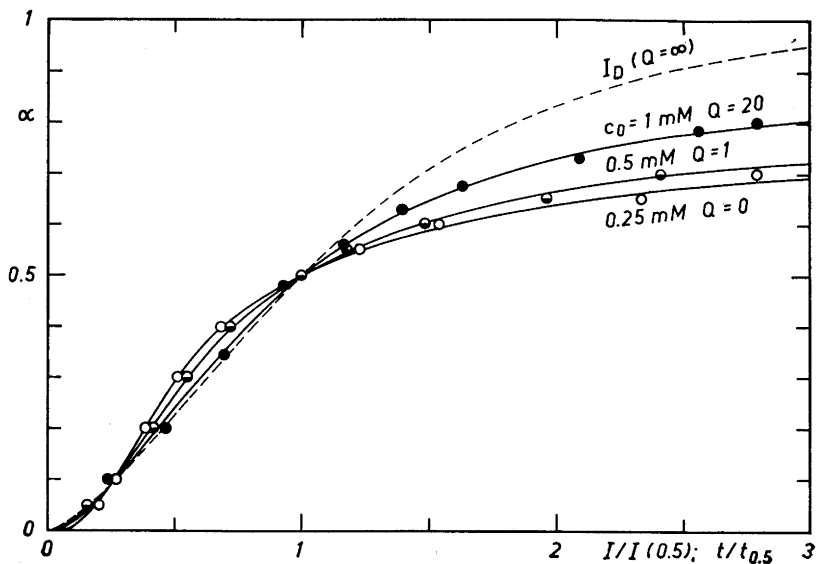


Fig. 4. Experimental values from BaSO_4 -precipitations with different initial concentration c_0 , and theoretical I_{DQ} -curves. All t - and I -values are divided by the corresponding value at $\alpha = 0.5$ in order to make it easier to see the characteristic differences in shape of the curves with different values of Q . Large c_0 corresponds to large Q , *i. e.* diffusional slow-down is more important at high than at small c_0 .

In Fig. 6 is shown how the concentration c' at the surface varies with time and how its deviation from c influences the kinetics.

If r_1 or N (the number of particles per unit volume) is known one may derive D and k_p from Q and $t_{0.5}$ by means of

$$\begin{aligned} K_p &= t_{0.5}/I_{pDQ}(0.5) \\ K_D &= t_{0.5}/I_{DpQ}(0.5) = QK_p \\ r_1 &= (3vc_0/4\pi N)^{1/3} \\ k_p &= r_1/3vc_0^2K_p = 1/(36\pi v^2N)^{1/3}c_0^{-1/3}K_p \\ D &= r_1^2/3vc_0K_D = 1/(48\pi^2vN^2c_0)^{1/3}K_D \end{aligned}$$

$I_{pDQ}(0.5)$ may be found from Fig. 5 also for values of Q not given in Table 1.

In the previous paper D was found for BaSO_4 from the initial slope of a plot of I_D against t , and k_4 was found as the final slope ($0.70 < \alpha < 0.80$) of I_4 against t . In this way the diffusion coefficient of BaSO_4 at 25°C was found to be $3.0 \times 10^{-6} \text{ cm}^2/\text{s}$.

If we plot α as a function of $\log t$ and determine Q and $t_{0.5}$ from Fig. 3 as described above, we get the values for D and k shown in Fig. 7. At 25°C , $D = 1.7 \times 10^{-5} \text{ cm}^2/\text{s}$.

The diffusion coefficient of BaSO_4 in aqueous solution has never been measured before (as far I know) because of the low solubility of this substance,

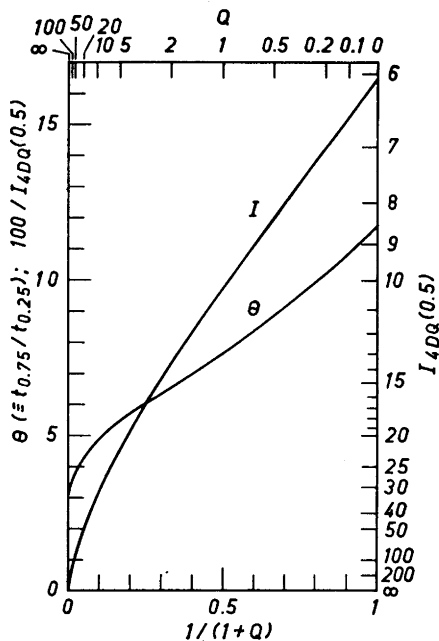


Fig. 5. Diagram for finding Q and $I_4DQ(0.5)$ from the ratio $\Theta \equiv t_{0.75}/t_{0.25}$.

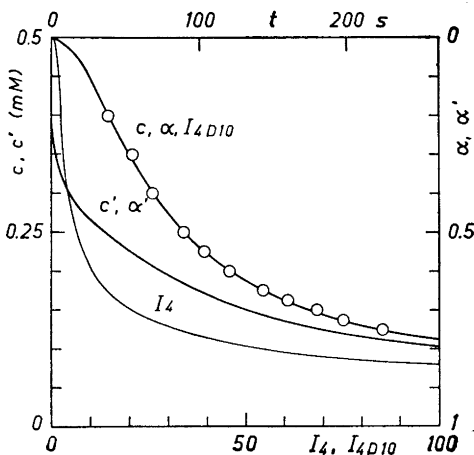


Fig. 6. The circles are experimental points and I_4D_{10} is the corresponding theoretical curve. c' is the concentration at the surface, calculated for the actual experiment. I_4 is the hypothetical curve obtained if diffusion did not slow down the reaction (i. e. $D = \infty$), for the same value of k_4 .

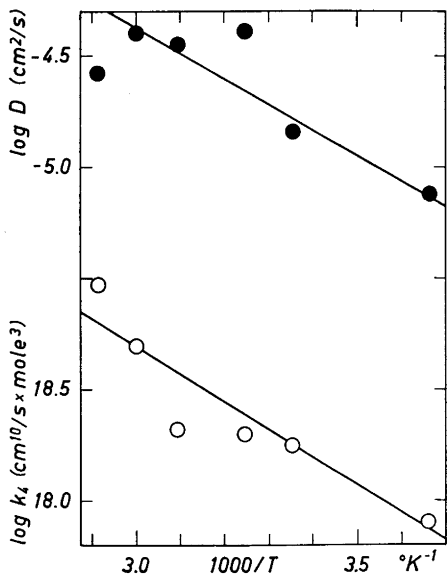


Fig. 7. The fourth-order rate constant of the crystal growth surface reaction and the diffusion coefficient plotted logarithmically as functions of the reciprocal temperature. The slopes give the heats (or energies) of activation, $-2.30 R d \log k_4/d(1/T) = 5000$ cal/mole for each of the curves.

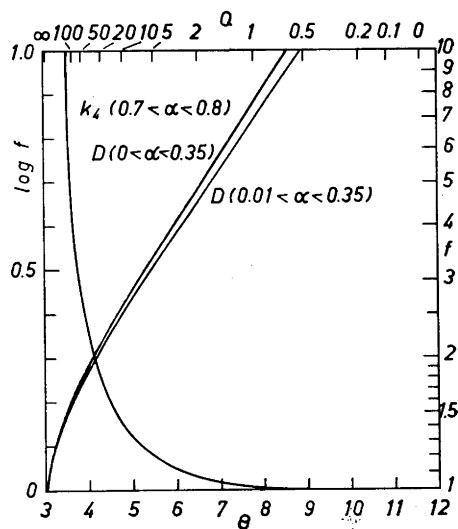


Fig. 8. The correction factors to be applied to the approximate values of D and k_4 obtained from the initial and final slopes on plots of t versus I_D and I_4 , respectively. The two curves for D correspond to drawing the straight line through origo and to approximating the points around the point of inflexion (practically all of the points with $0.01 < \alpha < 0.35$).

but it may be estimated rather accurately from the electric mobilities³, which gives $D = 9.4 \times 10^{-6}$ cm²/s. The value found by means of I_{pDQ} is seen to be better than the one obtained in the previous paper from I_D .

In Fig. 8 are given the correction factors to be applied to the (approximate) values determined by the method of the previous paper in order to get the correct ones. We observe that the correction factors are both equal to 2 for $Q = ca. 30$, and when one of them is smaller than 2 the other one is larger.

The error introduced by treating the crystals geometrically as spheres is not serious compared with the uncertainty of the experiments reported. When the measuring technique has been improved it may be necessary to correct for this shape-error through solving the Laplace equation of diffusion in the space around the crystal.

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