The Kinetics of Crystal Growth in Barium Sulfate Precipitation

II. Temperature Dependence and Mechanism *

ARNE E. NIELSEN

Universitetets fysisk-kemiske institut, Copenhagen, Denmark

The chronometric integrals (chronomals) for precipitation processes with time-independent particle number concentrations are solved, and a table of their numerical values is calculated.

The diffusion coefficient of $BaSO_4$ and the fourth order rate constant of crystal growth in $BaSO_4$ precipitation are determined from experiments at a range of temperatures between 0 and 70°C.

The dissociation of $2-2$ electrolytes in aqueous solution is discussed with special regard to $BaSO_4$.

A number of formally possible rate-determining mechanisms are discussed and four of them found to be in agreement with the experiments.

The results are compared with the Volmer-Becker-Döring and the Frank-Cabrera-Burton theories of crystal growth and are found to be in agreement with the former, but not the latter of these, *i. e.* the rate is governed by the formation of surface nuclei requiring a supersaturation ratio of about 10 or more in order to proceed at appreciable speed.

I. THEORETICAL PART; PRECIPITATION CHRONOMALS

1. Introduction. During the precipitation from a supersaturated solution the number of particles may either be constant or change with time. Here we shall only discuss cases where the number of particles is constant [1-10]. It follows that provided the solution is properly stirred the particles will grow with the same rate and be equally large. This has been observed with many sparingly soluble salts.

We shall first derive kinetic equations for precipitation, stating explicitly the constants of proportionality in terms of quantities such as the number of particles, the initial concentrations and the molar volume of the precipitating matter, and fundamental rate-constants. Then we will discuss how these quantities may be obtained from experiment and from theory.

---

* Part I. of this work, Ref.[1].

These methods will then be applied to the data from experiments on barium sulfate. Several mechanisms are suggested and compared to the experimental results. At last the results of this investigation will be compared to the accepted theories of crystal growth.

2. *Derivation of the kinetic equations.* If the rate of particle growth during precipitation from a supersaturated solution is controlled by the diffusion from the bulk of the solution to the surface of the particles we have [1,5,6,11].

$$\mathrm{d}r/\mathrm{d}t = vD(\mathrm{d}c/\mathrm{d}\varrho)_{\varrho=r}$$

where r is the radius of the particle or, if it is not a sphere, of a sphere of approximately the same volume as the particle, t the time, v the molar volume of the material, D the diffusion coefficient, c the concentration in mole/cm^3, and ϱ the distance from the center of the particle. Smoluchowski [12] showed that

$$(\mathrm{d}c/\mathrm{d}\varrho)_{\varrho=r} = (c-s)\,/\,r$$

where s is the solubility of the material. If we introduce the degree of reaction α by means of

$$1-\alpha = (c-s)\,/\,(c_o-s)$$

where c_o is the concentration at $t = 0$, we may write

$$\mathrm{d}r/\mathrm{d}t = vD(c-s)\,/\,r = vD(c_o-s)\,(1-\alpha)\,/\,r$$

Since now

$$r = r_\infty \cdot \alpha^{1/3}$$

where r_∞ is r at $t = \infty$, we have

$$(\mathrm{d}r/\mathrm{d}t =)$$
$$(1/3)r_\infty\alpha^{-2/3}\mathrm{d}\alpha/\mathrm{d}t = vD(c_o-s)\,(1-\alpha)/r_\infty\alpha^{1/3}$$
$$\mathrm{d}\alpha/\mathrm{d}t = 3vD(c_o-s)\alpha^{1/3}\,(1-\alpha)/r_\infty^2$$
$$\therefore t = r_\infty^2 I_\mathrm{D}/3v(c_o-s)$$

where

$$I_\mathrm{D} \equiv \int_o^\alpha \alpha^{-1/3}(1-\alpha)^{-1}\mathrm{d}\alpha$$

If the rate of growth is controlled by a reaction of the order p in the surface of the particle [13-15], with the rate constant k_p (mole/cm$^2 \cdot$ s) (mole/cm^3)$^{-p}$

$$\mathrm{d}r\,/\,\mathrm{d}t = vk_pc^p$$

We then have (when $c \gg s$)

$$(\mathrm{d}r/\mathrm{d}t =)\ (1/3)r_\infty\alpha^{-2/3}\mathrm{d}\alpha/\mathrm{d}t = vk_pc_o^p(1-\alpha)^p$$
$$\therefore t = r_\infty I_p/3vk_pc_o^p$$

where

$$I_p \equiv \int_{o}^\alpha \alpha^{-2/3}(1-\alpha)^{-p}\mathrm{d}\alpha$$

Frisch and Collins [11] solved the problem of mixed diffusion and first order surface reaction. In our terminology the solution may be obtained thus: let the concentration be c' at the surface of the crystal; then

$$\mathrm{d}r/\mathrm{d}t = (1/3)r_\infty\alpha^{-2/3}\mathrm{d}\alpha/\mathrm{d}t = vD(c_o(1-\alpha)-c')/r_\infty\alpha^{1/3} = vk_pc'^p$$

By elimination of c' one gets, for all values of p

$$\frac{d\alpha}{dt} = 3vk_p r_\infty^{-1}\alpha^{\frac{1}{3}}\left[c_o(1-\alpha) - \frac{r_\infty^2}{3vD\alpha^{\frac{1}{3}}} \cdot \frac{d\alpha}{dt} \right]^p$$

For $p = 1$ this can be reduced to

$$\frac{dt}{d\alpha} = \frac{r_\infty^2}{3vDc_o(1-\alpha)\alpha^{\frac{1}{3}}} + \frac{r_\infty}{3vk_1 c_o(1-\alpha)\alpha^{\frac{1}{3}}}$$

with the solution

$$t = \frac{r_\infty^2 I_D}{3vDc_o} + \frac{r_\infty I_1}{3vk_1 c_o}$$

which is the sum of the solutions to the "pure" problems. For $p \neq 1$ the solution is not simply the sum of the corresponding expressions.

Sometimes it is convenient to use the length l of the edge in a cube of the same volume as the particle rather than r. In case of diffusional rate control it is reasonable to substitute r_∞ by means of

$$(4/3)\pi r^3 = l^3$$

giving

$$t = l_\infty^2 I_D / \sqrt[3]{48\pi^2}\ vD(c_o-s)$$

In case of a surface reaction we may use

$$dl/dt = 2vk_p c^p$$
$$l = l_\infty \alpha^{\frac{1}{3}}$$

from which follows

$$(dl/dt =)\ (1/3)l_\infty \alpha^{-\frac{2}{3}}d\alpha/dt = 2vk_p c_o^p(1-\alpha)^p$$
$$d\alpha/dt = 6vk_p l^{-1}c_o^p \alpha^{\frac{2}{3}}(1-\alpha)^p$$

and

$$t = l_\infty I_p/6vk_p c_o^p$$

If the number of particles N per unit volume is known instead of r_∞ or l_∞ we may use

$$l_\infty^3 = v(c_o-s) / N$$

and obtain

$$t = I_D / D\sqrt[3]{48\pi^2 v(c_o-s)N^2}$$

and, respectively (for $c \gg s$)

$$t = I_p / 6v^{\frac{1}{3}}k_p c_o^{p-\frac{1}{3}}N^{\frac{1}{3}}$$

These two formulae are only exact for spheres and cubes, respectively, but may be applied without serious errors to particles of highly compact shape. In case of thin plates, needles or "star-like" crystals as are often met with in electrolyte precipitation experiments the formulae can be expected to give only the right order of magnitude.

3. *Formulae, numerical values.* The integrals I_D and I_p have been calcula-ted by numerical integration [5,8]. I_D was expressed by analytic functions by LaMer and Dinegar [6]. The mixed case of I_D and I_1 was similarly solved by Frisch and Collins [11]. Formulae for I_D and I_p (with any positive integer p) may be found by substituting a new variable for $\alpha^{1/3}$, decomposing, and using standard methods of integration. We introduce for brevity the two functions of α

$$L = \ln \frac{\sqrt{1 + \alpha^{1/3} + \alpha^{2/3}}}{1-\alpha^{1/3}} = \tfrac{1}{2} \ln \frac{1-\alpha}{(1-\alpha^{1/3})^3}$$

$$T = \sqrt{3}\ \mathrm{arctg}\ \frac{\sqrt{3}}{1 + 2\alpha^{-1/3}}$$

(arctg is the inverse tangent, sometimes denoted $\tan^{-1}$). The integrals can then be written

$$I_D = L - T$$
$$I_1 = L + T$$
$$I_2 = \frac{\alpha^{1/3}}{1-\alpha} + \frac{2}{3} I_1$$
$$I_3 = \frac{\alpha^{1/3}(8-5\alpha)}{6(1-\alpha)^2} + \frac{5}{9} I_1$$
$$I_4 = \frac{\alpha^{1/3}(41-52\alpha + 20\alpha^2)}{27(1-\alpha)^3} + \frac{40}{81} I_1$$
$$I_5 = \frac{\alpha^{1/3}(532-1\,023\alpha + 792\alpha^2-220\alpha^3)}{324(1-\alpha)^4} + \frac{110}{243} I_1$$
$$I_6 = \frac{\alpha^{1/3}(4\,210-10\,885\alpha + 12\,705\alpha^2-7\,084\alpha^3 + 1540\alpha^4)}{2\,430(1-\alpha)^5} + \frac{308}{729} I_1$$

Numerical values of I_D, I_1, I_2, I_3 and I_4 are given in Table 1. L and T may be found from the table by using

$$L = (I_1 + I_D)/2$$
$$T = (I_1 - I_D)/2$$

The coefficients in the general expression for I_p,

$$I_p = \frac{a_{p,1}\alpha^{1/3} + a_{p,2}\alpha^{1+1/3} + \ldots + a_{p,p-1}\alpha^{p-2+1/3}}{(1-\alpha)^{p-1}} + b_p I_1$$

can be found by solving the linear equations

$$\tfrac{1}{3}a_{p,1} = 1 - b_p$$

$$(i-\tfrac{2}{3})a_{p,i} + (p-i+\tfrac{2}{3})a_{p,i-1} = (-1)^i \binom{p-1}{i-1} b_p, \quad i = 2,3 \ldots p-1$$

$$\tfrac{2}{3}a_{p,p-1} = (-1)^p b_p$$

where

$$\binom{p-1}{i-1} = \frac{(p-1) \ \ldots \ (p-i+1)}{2 \cdot 3 \ \ldots \ldots \ (i-1)}$$

Table 1. The precipitation chronomals.

a	I_D	I_1	I_2	I_3	I_4
0.0001	0.00323	0.13925	0.1393	0.1393	0.1393
0.0003	0.00672	0.20084	0.2009	0.2009	0.2009
0.001	0.01501	0.30008	0.3001	0.3002	0.3003
0.003	0.03124	0.43299	0.4333	0.4337	0.4340
0.01	0.06990	0.64795	0.6496	0.6512	0.6529
0.03	0.14659	0.93928	0.9466	0.9540	0.9614
0.05	0.20778	1.11943	1.1341	1.1492	1.1647
0.10	0.33696	1.42943	1.4686	1.5104	1.5548
0.15	0.45155	1.65949	1.7314	1.8106	1.8978
0.20	0.56005	1.85382	1.9669	2.0960	2.2438
0.25	0.66620	2.02854	2.1922	2.3868	2.6194
0.30	0.77234	2.19183	2.4175	2.6977	3.0485
0.35	0.88009	2.34863	2.6500	3.0423	3.5596
0.40	0.99114	2.50263	2.8965	3.4370	4.1922
0.45	1.10686	2.65657	3.1644	3.9036	5.0051
0.50	1.22901	2.81312	3.4628	4.4731	6.0927
0.55	1.35960	2.97499	3.8040	5.1931	7.6131
0.60	1.50122	3.14530	4.2055	6.1403	9.8509
0.65	1.65737	3.32791	4.6936	7.4469	13.3541
0.675	1.74238	3.42542	4.9827	8.3047	15.8998
0.700	1.83304	3.52814	5.3118	9.3593	19.2811
0.725	1.93048	3.63722	5.6915	10.6825	23.8943
0.750	2.03596	3.75396	6.1369	12.3826	30.3893
0.775	2.15128	3.88019	6.6692	14.6297	39.8844
0.800	2.27882	4.01828	7.3204	17.7043	54.4171
0.825	2.42192	4.17160	8.1404	22.0962	77.9742
0.850	2.58542	4.34506	9.2118	28.7269	119.0924
0.875	2.77694	4.54623	10.6825	39.5090	198.357
0.900	3.00909	4.78777	12.8467	58.9801	374.256
0.925	3.30564	5.09345	16.3869	100.2645	858.979
0.950	3.71983	5.51652	23.3387	216.058	2 813.51
0.960	3.94639	5.74658	28.4932	332.021	5 433.07
0.970	4.23748	6.04112	37.0240	580.797	12 737.23
0.980	4.64633	6.45340	53.9667	1 286.58	42 530.6
0.990	5.34284	7.15329	104.4344	5 070.31	336 725
0.995	6.03767	7.84980	204.899	20 137.4	2 680 115
0.999	7.64846	9.46189	1 005.97	500 672	333 667 227

The first and the last equation are *not* obtained by letting $i = 1$ and $i = p$ in the formula given for $i = 2, 3, \ldots p{-}1$.

It is easily proved that for $p > 1$

$$\sum_{i=1}^{p-1} a_{p,i} = \frac{1}{p{-}1}$$

which constitutes a check on the numerical calculations.

4. The evaluation of kinetic constants. The best method of treating the data is probably to plot I_D or I_p as a function of the (through a) corresponding experimental time [8]. If the measurements are in accordance with the assump-

tions behind the 'I' chosen a straight line through origo is obtained. In some cases the reaction is diffusion controlled in the beginning and becomes, e. g., fourth order later on. Then a curved curve is obtained which gradually straightens and eventually approaches an asymptote of well defined slope. Both when the whole curve and when only a part of it is a straight line the diffusion coefficient or the rate constant may be calculated by means of the following equations.

$$D = (dI_D/dt)l_\infty^2 \;/\; (48\pi^2)^{1/3}v(c_o{-}s)$$
$$= (dI_D/dt) \;/\; (48\pi^2v(c_o{-}s)\;N^2)^{1/3}$$
$$= (dI_D/dt) \;/\; 7.795(v(c_o{-}s)N^2)^{1/3}$$
$$k_p = (dI_p/dt)l_\infty \;/\; 6vc_c^p$$
$$= (dI_p/dt) \;/\; 6v^{1/3}c_o^{p-1/3}N^{1/3}$$

l_∞ may be found by measuring the particles under microscope. In the experiments reported below N was found by counting at least 100 particles on a blood cell counting chamber under microscope. Another possible procedure would be to determine the sedimentation velocity according to Odén [16] or Andreasen [17]. In a certain range of sizes the turbidity may be taken proportional to the surface [18], which would also give the required information if the constant of proportionality is known. It is safest, however, in all cases to examine the particles under microscope in order to be sure whether they are compact enough to justify the assumptions made in deriving the formulae.

II. EXPERIMENTAL PART. THE DIFFUSION COEFFICIENT AND THE RATE CONSTANT FOR BaSO₄

1. *Introduction.* Previously it was found [1] that at 22°C the rate of growth of BaSO₄ may be expressed by

$$dl \;/\; dt = 630 \; c^4 \; m\mu/s \quad \text{for } c < 0.3 \text{ mM}$$

where l is the length of the edge in a cube of the same volume as the crystal. Dividing by twice the molar volume we get the rate of depositing matter on a unit of surface. Transforming into c-g-s-units we have

$$k_4 = 6.3 \times 10^{19} \;/\; 2 \times 51.9 = 6.1 \times 10^{17} \; (\text{mole/cm}^2\text{s}) \; (\text{cm}^3/\text{mole})^4$$

In Table 2 are shown some new and probably more accurate data for a range of temperatures. It was determined to use $c_o = 0.5$ mM because this gave the rates that could be measured best with the apparatus. With this c_o the rate is diffusion controlled in the first part and "surface-reaction"-controlled in the latest part of the experiment. Both D and k_4 can therefore be determined from the same run.

2. *Experimental.* The reacting aqueous solutions, 40 ml 1.00 mM BaCl₂ and 40 ml 1.00 mM Na₂SO₄ *(pro analysi)* were placed in an apparatus shown in Fig. 1, equilibrated in a thermostated water bath, and mixed by pressing the rubber ball. The electric conductance was measured as a function of time. The first reading was obtained 5 s after the moment of mixing. From measurements on solutions having the compositions of the reacting mixture at the degree of reaction a equal to 0.5 and 1.0, together with the value
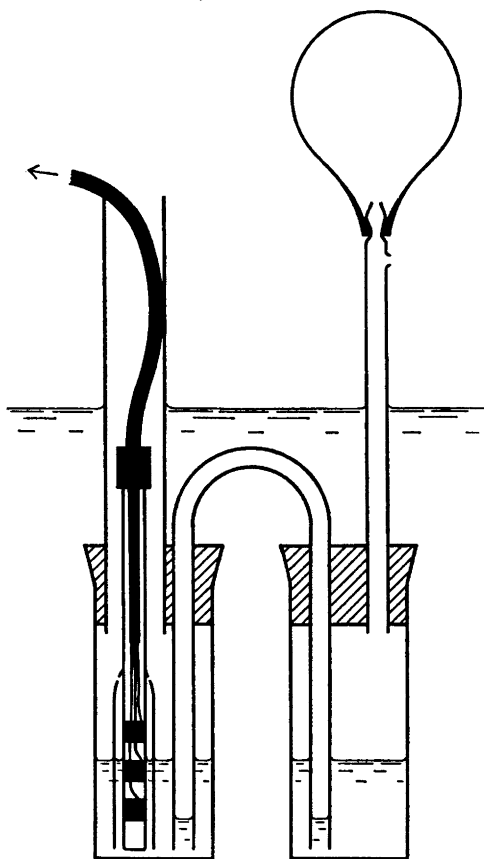
Fig. 1. The apparatus. The solutions were mixed by pressing the rubber ball. The arrow indicates the connection from the conductivity cell to the conductivity meter.

at $a = 0$ obtained in the kinetic experiment, a calibration curve was constructed for converting the electric conductance into a. The calibration curve was almost linear. The solution was frequently stirred by transferring it from one to the other of the two glasses. Afterwards a sample was placed on a counting plate and at least 100 particles were counted under microscope.

3. Numerical treatment. D was calculated by means of

$$D = (\mathrm{d}I_D/\mathrm{d}t) \ / \ (48\pi^2 v(c_o - s)N^2)^{1/3}$$
$$= (\mathrm{d}I_D/\mathrm{d}t) \ / \ 7.795(vc_oN^2)^{1/3}$$
$$= (\mathrm{d}I_D/\mathrm{d}t) \ / \ 0.231 \ N^{2/3}$$

For $\mathrm{d}I_D/\mathrm{d}t$ was used the initial slope on a graph of I_D *versus t*. See Fig. 2 and Table 3.

k_4 was calculated by means of

$$k_4 = (\mathrm{d}I_4/\mathrm{d}t) \ / \ 6v^{2/3}c_o^{4-1/3}N^{1/3}$$
$$= (\mathrm{d}I_4/\mathrm{d}t) \ / \ 6.58 \times 10^{-22}N^{1/3}$$

Table 2. Time in seconds (interpolated) as a function of a, from experiments with $c_0 = 0.5$ mM, at different temperatures.

a	$t=0$	25	35	50	60	70°C
0.05	25	14		10.5		
0.1	50	24	17	15.5	22.5	11
0.2	102	37	43	25.5	38	16
0.3	154	49	62	37	53	20
0.4	217	64	85	49	68	24
0.5	293	85	116	65	89	31
0.55	330	105	138	75	103	36
0.6	376	132	169	91	120	42
0.65	450	170	210	111	143	52
0.675	500	193	232	124	160	57
0.70	560	215	268	143	180	64
0.725	640	243	310	165	198	72
0.75	740	283	366	205	225	80
0.775		340	444	250	300	97
0.80		430	560	420	360	125

where dI_4/dt was found graphically on a plot of I_4 *versus* t, using the straight-line part of the curve for large t. See Fig. 2 and Table 3.

4. *Results.* In Fig. 3 $\log D$ is plotted as a function of $1/T$. From the slope $d\log D/d(1/T) = -1\,080$ one finds the heat of activation for the diffusion process $\Delta H_D^{\ddagger} = 5\,000 \pm 500$ cal/mole‡. In the same figure is also plotted the logarithm of the fluidity of pure water. It is seen that the heat of activation of diffusion is a little greater than that of the fluidity. This is what one would expect, because of the hydration of the ions.

Fig. 3 also shows $\log k_4$ against $1/T$. $-d\log k_4/d(1/T) = 1\,100$ which corresponds to the apparent heat of activation

$$\Delta H_A = 5\,000 \pm 500 \text{ cal/mole.}$$

A ten degree rise in temperature increases k_4 about one-third.

This may be compared to the value for crystal growth in magnesium oxalate precipitation obtained by Lichstein and Brescia [19], $\Delta H_A = 3$ kcal/mole, although they used a different theory [20] involving a first order constant.

Table 3. D and k_4, from N and data in Table 2 (see Fig. 2).

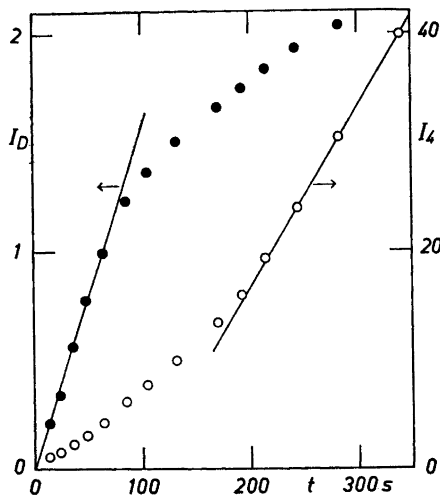| t °C	N 10^6cm^{-3}	dI_D/dt s^{-1}	dI_4/dt s^{-1}	D 10^{-6}cm^2/s	k_4 10^{18}cm^{10}/s · mole^3
0	1.81	0.0070	0.051	2.04	0.69
25	3.38	0.0157	0.160	3.02	1.68
35	0.66	0.0125	0.110	7.15	1.92
50	2.16	0.028	0.170	7.25	2.01
60	0.30	0.0146	0.160	14.1	3.63
70	2.76	0.050	0.544	11.0	5.88

Fig. 2. I_D and I_4 as function of the experimentally determined times at 25°C. From the slope of the straight-line parts of the curves the diffusion coefficient and the fourth-order velocity constant were determined.
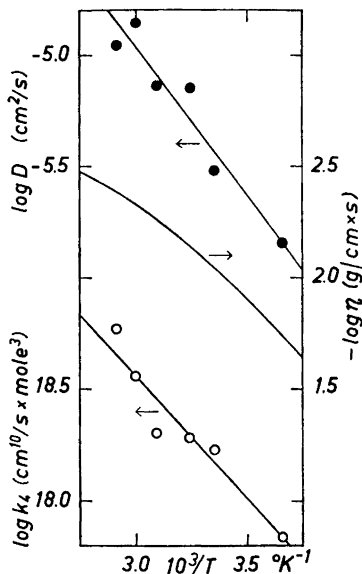
Fig. 3. Diagram for determination of the apparent heat of activation for diffusion of BaSO$_4$ and for the surface reaction of BaSO$_4$ crystal growth. In the middle is plotted for comparison the logarithm of the fluidity ($1/\eta$) of pure water.

III. THE DISSOCIATION OF 2—2 ELECTROLYTES

Before discussing these results we will consider the composition of the system. It is generally recognized that 2—2 electrolytes are only partly dissociated in aqueous solution [21,22]. For sulfates of bivalent metals we define

$$K_1 = (M^{++}) \, (SO_4^{--}) \, / \, (MSO_4)$$
$$K_2 = (MSO_4) \, (SO_4^{--}) \, / \, (M(SO_4)_2^{--})$$
$$K_3 = (M^{++}) \, (M(SO_4)_2^{--}) \, / \, ((MSO_4)_2)$$
$$K_4 = (M^{++})^2(SO_4^{--})^2 \, / \, ((MSO_4)_2) = K_1K_2K_3$$

The interpretation of experimental data from activity-, conductance- or cryoscopic measurements on dilute solutions for finding the K's is very uncertain, since the effects of the interionic forces masks the effects of the incomplete dissociation, and only approximate values of K_1 have been obtained this way.

The difficulty has however been solved by Kenttämaa [23] who measured the freezing point depression of CuSO$_4$, ZnSO$_4$, NiSO$_4$ and MgSO$_4$ in eutectic (cryohydratic) mixtures of water and a salt; the salts used were KNO$_3$, KClO$_3$ and KClO$_4$. Because of the presence of electrolytes in a roughly constant concentration even in the "pure solvent" the depressions may be extrapolated to infinite dilution of the 'MSO$_4$' in question without taking the interionic forces

into account. From the law of mass action it follows that if m_s denotes the stoichiometric concentration of the added electrolyte and Σm_i the sum of the concentrations of all the ions and molecules that are not common with those arising from the saturating electrolyte, the function $\overline{\varphi}$ defined by

$$\overline{\varphi} = (2m_s - \Sigma m_i) \,/\, (\Sigma m_i - m_s)^2$$

satisfies

$$\overline{\varphi} = 1/K_1 + \Sigma m_i/K_1 K_2$$

Σm_i and thereby also $\overline{\varphi}$ are found from the freezing point depressions.

From a plot of $\overline{\varphi}$ *versus* Σm_i K_1 and K_2 may be obtained. K_1 is strongly dependent on the ionic strength I, whereas K_2 may be regarded — in a first approximation — as independent of the salt concentration. Kenttämaa did not give K_2 explicitly, but it is easily found from the reported values of the coefficient in the linear expression for $\overline{\varphi}$.

All values of K_2 lie between 0.1 and 0.25, most of them close to 0.15 M. At $I = 0$, pK_1 ranges between 2.186 and 2.294 for the four sulfates of bivalent metals investigated by Kenttämaa. In our experiments on $BaSO_4$ precipitation $I = 0.002$ in the part of the experiment which is used for determination of k_4. At $I \cong 0.002$ the correction to pK_1 is about —0.16; we may take $pK_1 = 2.1$, $K_1 = 0.008$ mole/l as a representative value.

Since the dissociation constants seem to be the same for all sulfates of bivalent metals, we may apply them to $BaSO_4$ as well.

This conclusion may seem a little too risky. Since $BaSO_4$ is only 10^{-5} as soluble as the sulfates on which K_1 and K_2 were measured one would perhaps expect it to be appreciably less dissociated. This is however not the case. The calibration curves mentioned in the experimental part of this article turned out to be very near to straight lines. Actually the conductivity at $\alpha = 0.5$ was higher than the arithmetic mean of the conductivities at $\alpha = 0$ and $\alpha = 1$ by about 2.5 % of the total change, *i. e.*

$$e \equiv (\varkappa_{0.5} - (\varkappa_0 + \varkappa_1)\,/\,2)\,/\,(\varkappa_0 - \varkappa_1) = 0.025$$

The curvature is due partly to interionic forces and partly to the incompleteness of the dissociation
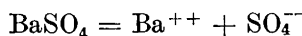
$$BaSO_4 = Ba^{++} + SO_4^{--}$$

with the dissociation constant

$$K_1 = (Ba^{++})\,(SO_4^{--})\,/\,(BaSO_4) = c\delta^2\,/\,(1-\delta) = c_o\,(1-\alpha)\delta^2\,/\,(1-\delta)$$

where δ is the degree of dissociation. If we neglect for the moment the interionic forces but not the incompleteness of the dissociation we get

$$\varkappa_\alpha = \Lambda^o_{BaSO_4} c_o(1-\alpha)\delta + \varkappa_1$$
$$e \equiv (\delta_{0.5} - \delta_o)\,/\,2\delta_o$$
$$\delta_{0.5}/\delta_o = q \equiv 1 + 2e$$
$$K_1\,/\,c_o = \delta_o^2\,/\,(1-\delta_o) = 0.5\delta_{0.5}^2\,/\,(1-\delta_{0.5})$$
$$\qquad\quad = q^2\delta_o^2\,/\,2(1-q\delta_o)$$
$$\delta_o = (2-q^2)\,/\,(2q-q^2)$$
$$K_1 = c_o(2-q^2)^2\,/\,(2q-q^2)\,(2q-2)$$
$$\quad = c_o(1-4e-4e^2)^2\,/\,(1-4e^2)4e$$
$$\quad \cong c_o(1/4e-2) = 0.0005 \times 8 = 0.004 \text{ mole/l}$$

Since the interionic forces also tend to diminish the electric conductivity and thus contribute positively to e, the value found for K_1 is a minimum value; we therefore only know that for $BaSO_4$

$$K_1 > 0.004 \ mole/l$$

but this is entirely in agreement with the assumption that K_1 has the same value for $BaSO_4$ as for the highly soluble sulfates of bivalent metals, i. e. $K_1 = 0.008$ mole/l. It is less certain to put $K_2 = 0.15$ for $BaSO_4$ because it is that much in case of the highly soluble sulfates, but there is no reason to assume it is wrong by more than, e. g., a factor of ten. K_3 is entirely unattainable from Kenttämaas experiments since the function $\bar{\varphi}$ was found to depend lineary on $\varSigma m_i$. If we assume that the experimental uncertainty allows for a maximum concentration of $(MSO_4)_2$ equal to $M(SO_4)_2^-$ at the highest concentration of MSO_4 used, we find from the mass action law

$$K_3 = (M^{++})(M(SO_4)_2^-) \ / \ ((MSO_4)_2) > (M^{++}) = 0.2 \ mole_l.$$

For $BaSO_4$ of course K_3 may be less. For the highly soluble sulfates we have now

$$K_4 = K_1 K_2 K_3 > 0.008 \times 0.15 \times 0.2 = 2 \times 10^{-4} M^3 = 2 \times 10^{-13} \ mole^3/cm^9$$

IV. THE RATE-DETERMINING MECHANISM IN $BaSO_4$ CRYSTAL GROWTH

Since the activation energy of the fourth order crystallization reaction is nearly the same as the activation energies of $BaSO_4$ diffusion and of viscous flow of pure water, the rate-determining step is a reaction in which almost any close approach between two molecules of the reactants leads to reaction.

If the collision number of the reactants — when supposed not to react — is Z collisions per unit of volume (or surface) and time, calculated from simple gas theory, we may write the rate of the reaction

$$J = Z\exp(-\varDelta G^{\ddagger}/RT)$$

where $\varDelta G^{\ddagger}$ is the standard activation free energy change, and $\exp(-\varDelta G^{\ddagger}/RT)$ is the ratio between the number of collisions leading to reaction and the number of collisions between the reactant molecules if no reaction took place.

In a liquid two molecules subject to an encounter have a rather large probability of repetitive encounters, performing some sort of oscillations, before a third molecule comes in between. If a reaction of activation free energy less than the activation free energy of diffusion can occur between the two colliding molecules, it is almost certain that it will happen rather than the two molecules depart. Therefore the free energy of activation of the reaction shall be replaced by the free energy of activation for diffusion, and the temperature dependence of the velocity is determined entirely by the enthalpy of activation for diffusion, and the change of Z with temperature. If we neglect any entropy change of activation for diffusion we have

$$J = Z\exp(-\varDelta H^{\ddagger}/RT)$$

where empirically $\Delta H^{\ddagger} \cong 5\,000$ cal/mole‡ if Z is not strongly temperature dependent; $\exp(-\Delta H^{\ddagger}/RT) = 10^{-4}$ at 0°C.

We will now discuss the following types of possible rate determining mechanisms.

(i) transport of matter from the solution to the crystal.
(ii) collision between molecules (or ions) from the solution and adsorbed molecules (ions).
(iii) triple collisions between two molecules (ions) and the crystal.
(iv) collision between adsorbed molecules.

Above $c = ca.$ 4×10^{-7} mole/cm^3 $(= 0.4$ mM) the rate determining mechanism has already been shown [1] to be the diffusion of BaSO$_4$ — mostly as ions — from the bulk of the solution to the surface. In the following we are going to discuss $c < 4 \times 10^{-7}$ mole/cm^3. As an example we will estimate the concentrations in a 0.1 mM $= 10^{-7}$ mole/cm^3 solution of BaSO$_4$. (The solubility is $ca.$ 10^{-8} mole/cm^3 at 25°C and $ca.$ 8×10^{-9} at 0°C; see Seidell [24] for references.)

If we assume the following orders of magnitude (at 0°C)·

$$K_1 = 10^{-5}, \ K_2 = 10^{-4}, \ K_3 = 10^{-4} \text{ mole/cm}^3$$

and, consequently $K_4 = 10^{-13}$ (mole/cm^3)^3 we find for $c = 10^{-7}$ mole/cm^3 the following concentrations:

$$(\text{Ba}^{++}) = (\text{SO}_4^{--}) = c = 10^{-7}, \ (\text{BaSO}_4) = 10^{-9},$$
$$(\text{Ba}(\text{SO}_4)_2^{--}) = 10^{-12} \text{ and } ((\text{BaSO}_4)_2) = 10^{-15} \text{ mole/cm}^3.$$

At this concentration we found experimentally $J = k_4 c^4 = 7 \times 10^{-11}$ mole/cm^{2}s.

If the rate is determined by the frequency of collisions between the crystal and molecules of concentration C and molecular weight M ($\sim$200 g/mole) the reaction rate per cm^2 is

$$J = C\sqrt{RT/\pi M} \ \exp(-\Delta H^{\ddagger}/RT) = 0.6 \times C$$

It follows that if this mechanism shall be rate determining

$$C = 7 \times 10^{-11}/0.6 = 10^{-10} \text{ mole/cm}^3$$

Since $((\text{BaSO}_4)_2)$ is only 10^{-15} mole/cm^3 it can not be the diffusion of $(\text{BaSO}_4)_2$ that is rate determining. It may however be the diffusion of BaSO$_4$-molecules. In order to get the right order (4) of the reaction only collisions with another BaSO$_4$-molecule at the surface may lead to growth. If one-tenth of the surface is covered by adsorbed BaSO$_4$-molecules in adsorption equilibrium with the ionic contents of the solution at $c = 10^{-7}$ mole/cm^3, the observed rate is obtained by this mechanism. Since the molar volume of BaSO$_4$ is 52 cm^3 this corresponds to a concentration of 1/520 mole/cm^3; which is $1/(520 \times 10^{-9})$ $= 2 \times 10^6$ times as high as in the solution. Another possible mechanism cf the same sort is the reaction between a colliding Ba^{++} ion and an adsorbed Ba(SO$_4$)$_2^{-}$ ion; only $10^{-10}/10^{-7} = 10^{-3}$ of the surface needs be covered by the reactive ionic species. Since the atoms of the (probably) linear $^-$SO$_4$BaSO$_4^-$ shall rearrange rather appreciably forming the (probably) square (BaSO$_4$)$_2$, there must be a rather low entropy of activation so that much more than 10^{-3}

of the surface must be covered, and the concentration at the surface must be more than about $(1/100) \times 10^{-3}/10^{-12} = 10^7$ times the concentration in the solution.

Triple collisions are difficult to define in a generally acceptable way. If we however count any encounter between two molecules or ions closer than a distance λ from the surface of the crystal as a triple collision, we may find the required λ by comparison with the experiment. The encounter may either occur between two $BaSO_4$ molecules or between a Ba^{++} and a $Ba(SO_4)_2^{--}$-ion. We have, respectively, the (simple gas theory) collision numbers

$$Z_{11} = 2n^2d^2\sqrt{\pi RT/M}$$

and

$$Z_{12} = n_1n_2d_{12}^2\sqrt{8\pi RT/\mu_{12}}$$

where

$$d_{12} = (d_1 + d_2)/2, \quad \mu_{12} = M_1M_2 / (M_1 + M_2)$$

With $M = 200$, $\mu = 100$, $d = d_{12} = 5$ Å $= 5 \times 10^{-8}$ cm we find at 0°C

$$Z_{11} = C^2 \times 5 \times 10^{13}$$
$$Z_{12} = C_1C_2 \times 10^{14} \text{ mole/cm}^2\text{s}$$

where C, C_1 and C_2 are measured in mole/cm^3. At $c = 10^{-7}$, $J_{\text{exp}} = 7 \times 10^{-11}$ mole/cm^{2}s; but

$$J = \lambda \times Z_{11} \times \exp(-\Delta H^{\ddagger}/RT)$$
$$= \lambda \times C^2 \times 5 \times 10^{13} \times 10^{-4} \text{ or } = \lambda \times C_1C_2 \times 10^{14} \times 10^{-4}$$

With $C = (BaSO_4) = 10^{-9}$ we find

$$\lambda = 7 \times 10^{-11}/5 \times 10^{-9} = 0.01 \text{ cm}$$

With $C_1 = (Ba^{++}) = 10^{-7}$, $C_2 = (Ba(SO_4)_2^{--}) = 10^{-12}$ we find

$$\lambda = 7 \times 10^{-11}/10^{-9} = 0.1 \text{ cm}$$

None of these mechanisms can therefore give the observed rate with a reasonable value of λ (which must, of course, be of molecular dimensions, $i.\ e.\ \lambda \sim 1$ Å).

In a two dimensional gas

$$Z_{11} = n^2d\sqrt{\pi RT/M}$$
$$Z_{12} = n_1n_2d_{12}\sqrt{2\pi RT/\mu}$$

where Z_{11} and Z_{12} are the numbers of collisions per cm^2 and s, between similar and different molecules, respectively, and n, n_1, n_2 are the surface concentrations in molecules per cm^2, other symbols having the same meaning as in the case of a three-dimensional gas. With $d = 5 \times 10^{-8}$ cm, $M = 200$, $\mu = 100$ we have

$$Z_{11} = n^2 \times 10^{-3}$$
$$Z_{12} = n_1n_2 \times 2 \times 10^{-3}$$
$$J = 7 \times 10^{-11} = Z_{11}\exp(\Delta H^{\ddagger}/RT)/N_A = n^2 \times 10^{-3-4}/6 \times 10^{23}$$
$$\therefore n = 2 \times 10^{10} \text{ cm}^{-2}$$

or from Z_{12}

$$\therefore n_1n_2 = 10^{20} \text{ cm}^{-4}$$

In a compact layer of $BaSO_4$ molecules $n =$ thickness $\times$ contents in 1 $cm^3 = d \times (1/v) \times N_A = 5 \times 10^{-8} \times 0.02 \times 6 \times 10^{23} = 6 \times 10^{14}$ cm^{-2}. The surface concentration necessary for the rate observed is only the fraction $2 \times 10^{10}/6 \times 10^{14} = 3 \times 10^{-3}$ of that of a compact layer. Calculated as volume concentration it is $2 \times 10^{10}/5 \times 10^{-8} = 4 \times 10^{17}$ molecules/cm^3 = $4 \times 10^{17}/6 \times 10^{23} = 10^{-6}$ mole/cm^3, $i.~e.$ 1 000 times as high as in the solution. This mechanism seems thus quite reasonable.

Finally, $n_1 n_2 = 10^{20}$ cm^{-4} corresponds to $C_1 C_2 = 10^{20}$ $(6 \times 10^{23})^{-2} =$ 3×10^{-28} $(mole/cm^2)^2 = 3 \times 10^{-28}/(5 \times 10^{-8})^2 = 10^{-11}$ $(mole/cm^3)^2$; in the solution $C_1 C_2 = (Ba^{++})~(Ba(SO_4)^{--}) = 10^{-7} \times 10^{-12} = 10^{-19}$ $(mole/cm^3)^2$; we see that if the concentrations in the surface are 10^4 as large as in the solution, this mechanism can give the right rate.

Conclusion. Four of the discussed mechanisms could give a fourth order reaction with the right rate constant.

Reaction

		c_{ads}/c_{soln}
(1) $BaSO_4(soln) + BaSO_4(ads)$	$\rightarrow$ crystal	2×10^6
(2) $Ba^{++}(soln) + Ba(SO_4)_2^{--}(ads)$	$\rightarrow$ »	$> 10^7$
(3) $2~BaSO_4(ads) \rightarrow$	»	10^3
(4) $Ba^{++}(ads) + Ba(SO_4)_2^{--}(ads)$	$\rightarrow$ »	$> 10^4$

If the differences between the four values of c_{ads}/c_{soln} are significant and if we rate a reaction as more probable than any other requiring a higher adsorption affinity to the crystal surface, in order to have the same velocity, we may point out reaction (3) as the dominating one, (4) as less important and (1) and (2) as practically negligible.

We have assumed that the ("apparent") activation energy $-Rd\ln k_4/d(1/T)$ was due entirely to the diffusion process. Since

$$k_4 = J/c^4 = (Z/c^4)\exp(-\Delta G^{\ddagger}/RT)$$

any dependence of Z on T will contribute as well. Since the collisions involve complex molecules or ions the enthalpy of association (= minus enthalpy of dissociation) is a part of the "apparent" activation energy. A change by a factor 10 in the ration c_{ads}/c_{soln} is necessary for every $RT\ln10 = 1~250$ cal of dissociation enthalpy. The heat of precipitation is about 5 000 cal/mole $BaSO_4$ (Muller [25] found 5 455 at 25°C; from National Bureau of Standards' "Selected Values ..."[26] one finds 4 630 cal/mole $BaSO_4$ (evolved).) The heat of dissociation of $BaSO_4$ is probably numerically less than this number. It may be zero if the energy change of "hydration" of the ions just compensates the work of the electric attraction forces.

V. COMPARISON WITH THE VOLMER-BECKER-DÖRING AND THE FRANK-CABRERA-BURTON THEORIES OF CRYSTAL GROWTH

1. *Introduction.* The theories of crystal growth have been developed primarily by Volmer and Weber [27,28], Farkas [29], Kaischew and Stranski [30], Becker and Döring [31], Cabrera and Burton [32,33] and Frank [33,34]. If the rate

of crystal growth is controlled by surface two-dimensional nucleation the rate is, according to Cabrera and Burton [32]

$$J = \nu ac \exp(-(U + A/3)/kT)$$

where

ν = "frequency of vibration" or $kT/h = 6 \times 10^{12}$ s^{-1},

a = a molecular dimension (diameter of an ion or thickness of an adsorbed layer),

c = concentration in the supersaturated solution,

U = energy of activation for diffusion,

$A = \gamma'^2\pi/kT\ln\alpha$ = free energy of formation of critical (circular!) surface nucleus,

γ' = edge (free) energy per molecule of the surface nucleus,

k = Boltzmann's constant,

T = temperature,

α = supersaturation ratio (ratio of c to the solubility).

The reason why the energy of activation shall enter in the formula with only one-third of its full value A, is that the bottle-neck of crystal growth rate controlled by surface nucleation is not the nucleus of maximum free energy, because this is formed by collisions between smaller embryos, but rather the formation of embryos of energy about one-third of the nucleus.

Usually an electrolyte crystal will grow with a measurable speed when α is greater than about 1.01 and this observation does not agree at all with the quoted formula. Therefore another mechanism with lower activation energy had to be found, and as shown by Frank [34] this is provided by dislocations. In the case of $BaSO_4$, however, the rate of growth is extremely slow when α is smaller than about 10. This indicates clearly that in $BaSO_4$ growth, surface nucleation may have a chance to be rate determining in stead of the Frank dislocation mechanism.

2. *The surface nucleus.* In order to examine this possibility we calculate the value of γ' consistent with the experimental J and α.

From the Cabrera-Burton-expression for J we derive

$$\ln J = \ln \nu ac - U/kT - \gamma'^2\pi/3k^2T^2\ln(c/s)$$
$$p = d\ln J/d\ln c = 1 + \gamma'^2\pi/3(kT\ln\alpha)^2 = 1 + n/3$$

where p is the order of the reaction and n the number of ions in the (equilibrium) surface nucleus. With $p = 4$, $T = 298°$K, $\alpha = 25$ we find

$$n = 3(p-1) = 9$$
$$\gamma' = \sqrt{n/\pi kT\ln\alpha} = 2.0 \times 10^{-13} \text{ erg}$$

3. *The surface tension.* It is crucial to this hypothesis whether the value of γ' is reasonable. This quantity is impossible to measure except through J, and difficult to calculate because the structures of the surface and of the surface nuclei are rather unknown. But perhaps it may be estimated from the surface tension γ by means of

$$\gamma' = a^2\gamma$$

where $a = 3.5$ Å is the distance between the centres of two neighbouring ions in the $BaSO_4$-lattice. This formula corresponds to the view that the free energy of the surface + nucleus can be calculated as the surface tension times the total surface area including that of the vertical wall of the nucleus of heigth a.

The surface tension of an ionic crystal in vacuum may be estimated from Born and Stern's formula [35]

$$\gamma = 0.1166e^2/\delta^3$$

(e = ionic charge, δ = lattice constant) although it was only derived for a NaCl-type crystal with electrostatic (Coulomb) forces of attraction and repulsion, and with a general repulsion between ions corresponding to a potential energy term proportional to the minus 9th power of distance. Substituting $e = z\varepsilon$, $\delta^3 = 4v/N$, where z = charge number, ε = electronic charge, v = molar volume and N = Avogadro's number we get

$$\gamma = 0.02915 \ z^2\varepsilon^2N/v$$

and for $BaSO_4$ ($z = 2$, $v = 51.9$ cm^3/mole) we obtain

$$\gamma = 312 \ erg/cm^2$$

This value (or, to precise 310) was claimed to agree with experiments on $BaSO_4$ by Bruzs [36], but it is not clear from the article how the agreement is substantiated.

The surface tension of $BaSO_4$ was determined by Hulett [37] and Dundon [38] from the dependence of solubility on particle size. In Hulett's article there were several errors in the calculation, as pointed out by Freundlich [39]. (Freundlichs recalculated value, $\gamma = 4\ 000$ erg/cm^2 is, however, also in error. The correct value was given by Dundon [38] and in later editions of Freundlichs book.[40]) According to Dundon, Hulett's measurements give 1 250 and her own 3 000 erg/cm^2, both numbers being rather uncertain, mainly because it is difficult to measure the particle size accurately.

Both Hulett and Dundon did only approach equilibrium through decreasing concentrations (measured by electric conductance), therefore the results may be too high by an unknown amount. There are at least two causes of experimental errors that can keep a too high concentration constant in time, 1) the stirring motion may "wear" on the crystals, so that small bits of higher solubility are broken off leading to a stationary non-equilibrium state with constant concentration, and 2) there may be a practical limiting supersaturation for growth, below which no further precipitation occurs. At low supersaturation $1/\ln a$ in the formulae for nucleus size and for the nucleation free energy becomes very large and the crystal growth becomes extremely slow. This must also lead to higher values than $p = 4$ in the rate equation, at lower concentrations than investigated in the present work.

(One might expect that the critical size and the kinetic order of the reaction both change gradually during the experiment; but since we are dealing with small numbers (< 20) we must pay attention to the fact that certain numbers (e. g. 4, 6 or 12) of ions can be arranged in configurations of much lower energy than other numbers (e. g. 5). Therefore the critical size must

be a discontinuous function (with large jumps) of the concentration, and may very well be a constant in the whole range investigated kinetically).

The works of Hulett and Dundon have been criticized by several authors; for references see the articles of Cohen and Blekkingh [41], who tried to approach equilibrium from "the other side". They dissolved finely powdered very pure barium sulfate in conductivity water, and claim that they did not succeed in transgressing the solubility of large crystals. (Perhaps they removed the supersaturation during the filtrations before the final measurements?)

As a consequence of these facts we will assume that the best choice for the surface tension of barium sulfate (even in contact with solution) is the theoretical value in vacuum 312 erg/cm². Therefore we find

$$\gamma' = 312 \times (3.5 \times 10^{-8})^2 = 3.8 \times 10^{-13} \text{ erg}$$

The disagreement between this value and the 2.0×10^{-13} erg required by the nucleation theory is not sufficient to reject the theory, since both values are calculated using very simplifying assumptions.

4. *The temperature dependence.* We still have to check whether the temperature dependence is in accord with the surface nucleation theory. The temperature dependence is expressed in the total (apparent) heat of activation. Assuming γ' but not s independent of T we derive

$$\Delta H_A = k \mathrm{dln}k_p \,/\, \mathrm{d}(1\,/\,T) = -k \mathrm{dln}(J\,/\,c^p)\,/\,\mathrm{d}(1\,/\,T)$$
$$= U + 2A\,/\,3 + (p\!-\!1)k \mathrm{dln}s\,/\,\mathrm{d}(1\,/\,T)$$
$$= kT\ln(vaca^{p-1}\,/\,J) - (p\!-\!1)\Delta H_s\,/\,2$$
$$= kT\ln(va\,/\,s^{p-1}k_p) - (p\!-\!1)\Delta H_s\,/\,2$$

ΔH_s is the heat of solution per molecule of $BaSO_4$. With $a = 3.5 \times 10^{-8}$ cm, $s = 10^{-8}$ mole/cm³, $p = 4$, $T = 298°K$ $k_4 = 1.7 \times 10^{18}$ cm¹⁰/s · mole³, $\Delta H_s = 4\,630$ cal/mole (Rossini *et al.*[26]) we find

$$kT\ln(va\,/\,s^{p-1}k_p) = 7.8 \times 10^{-13} \text{ erg} = 11\,000 \text{ cal/mole}$$
$$\Delta H_A = 11\,000 - 7\,000 = 4\,000 \text{ cal/mole}$$

in good agreement with the measured value, 5 000 cal/mole.

5. *The factor 1/3 on the activation energy.* As was mentioned earlier in this paper the reason why the energy of activation for surface nucleation shall enter in the formulae with only one-third of its value, is that the bottle-neck of crystal growth rate controlled by surface nucleation is not the formation of the nuclei of maximum free energy, but only of embryos with one-third of the critical energy, because these have greater probability for encounters with similar or larger molecules than for being dissolved. Cabrera and Burton [32] do not give all details of the proof of this essentiel theorem. Since however $BaSO_4$ provides an example of this sort of growth mechanism it is of interest to investigate if the theorem is obeyed. We identify the 'one-third surface nuclei' with adsorbed $(BaSO_4)_2$-molecules. Since adsorbed ionic species such as Ba^{++} and $Ba(SO_4)_2^{--}$ seem to have concentrations 10^4 as high in the adsorption layer as the same ions in the solution, we assume that the concentration of $(BaSO_4)_2$ is 10^8 times as high in the adsorption layer (of thickness 5 Å) as in

the solution. In the case subject to numerical estimates ($c_o = 10^{-7}$ mole/cm^3, 0°C) this amounts to

$$10^8 \times 10^{-15} = 10^{-7} \text{ mole/cm}^3$$

this is equivalent to

$c' = 5 \times 10^{-8} \times 10^{-7} = 5 \times 10^{-15}$ mole per cm^2 of the crystal surface.

The formula for collisions between like molecules in a two-dimensional layer is

$$Z_{11} = n^2 d\sqrt{\pi RT/M}$$

where n = number of molecules per cm^2 of the layer, d = collision diameter $\simeq$ 5×10^{-8} cm, M = molecular weight $\simeq 200$ g/mole. Substituting $n = Nc'$, dividing by N (Avogadros' number) and multiplying by the activation energy exponential function $\exp(-U/RT)$ for diffusion ($U \simeq 5\ 000$ cal/mole) we get the rate of collisions between $(BaSO_4)_2$-molecules in the adsorption layer:

$$J = (Z_{11}/N) \exp(-U/RT) = c'^2\ Nd\sqrt{\pi RT/M}\ \exp(-U/RT)$$
$$= (5 \times 10^{-15})^2 \times 6 \times 10^{-16} = 1.5 \times 10^{-12} \text{ mole}(BaSO_4)_2/\text{cm}^2\text{s}$$

Since this is of the same order of magnitude as the experimental rate of growth (7×10^{-11} mole $BaSO_4$/cm^{2}s) the theorem has been verified.

VI. CONCLUSION

We have arrived at the following view of crystal growth of barium sulfate. At low concentrations ($c <$ about 0.4 mM) the rate-determining step is the formation of adsorbed double-molecules $(BaSO_4)_2$ on the crystal surface. This is a fourth order reaction, and its rate is determined by the rate of diffusional (or "Brownian") movement of the smaller ionic or molecular species (Ba^{++} + $Ba(SO_4)_2^=$ or $BaSO_4 + BaSO_4$) against each other in an adsorbed layer on the crystal surface.

The critical size of the surface nucleus is calculated from simplifying assumptions to be about 9 ions; this is critical with respect to free energy, but not to rate. In contrast to most other crystals whose rate of growth has been investigated, $BaSO_4$ does not grow by the Frank dislocation mechanism, and requires consequently much higher supersaturation ratios ($\alpha > 10$) than the latter ($\alpha > 1.01$).

At high concentrations ($c >$ about 0.4 mM) the rate of growth is controlled by the diffusion of Ba^{++} and $SO_4^=$ ions from the bulk of the solution to the crystal surfaces as found in the first part[1] of this work.

REFERENCES

1. Nielsen, A. E. *Acta Chem. Scand.* **12** (1958) 951.
2. Odén, S. and Werner, D. *Arkiv Kemi, Mineral. Geol.* **9** (1925) No. 23.
3. Tovborg Jensen, A. *Z. physik. Chem.* **A180** (1937) 3.
4. Andreasen, A. H. M., Skeel-Christensen, K. and Kjær, B. *Kemisk Maanedsblad* **24** (1943) 93.
5. Wert, C. and Zener, C. *J. Appl. Phys.* **21** (1950) 5.

6. LaMer, V. K. and Dinegar, R. H. *J. Am. Chem. Soc.* **72** (1950) 4847.
7. Turnbull, D. *Acta Met.* **1** (1953) 684.
8. Nielsen, A. E. *J. Colloid Sci.* **10** (1955) 576.
9. Pacter, A. *J. Phys. Chem.* **62** (1958) 1025.
10. Doremus, R. H. *J. Phys. Chem.* **62** (1958) 1068.
11. Frisch, H. L. and Collins, F. C. *J. Chem. Phys.* **21** (1953) 2158.
12. v. Smoluchowski, M. *Z. physik. Chem.* **92** (1918) 129.
13. Christiansen, J. A. and Nielsen, A. E. *Z. Elektrochem.* **56** (1952) 465.
14. Johnson, R. A. and O'Rourke, J. D. *J. Am. Chem. Soc.* **76** (1954) 2124.
15. O'Rourke, J. D. and Johnson, R. A. *Anal. Chem.* **27** (1955) 1699.
16. Odén, S. *Kolloid-Z.* **18** (1916) 33.
17. Andreasen, A. H. M. and Lundberg, J. J. V. *Ber. deut. keram. Ges.* **11** (1930) 249.
18. Wells, P. V. *Chem. Revs.* **3** (1927) 331, p. 351.
19. Lichstein, B. and Brescia, F. *J. Am. Chem. Soc.* **79** (1957) 1591.
20. Peisach, J. and Brescia, F. *J. Am. Chem. Soc.* **76** (1954) 5946.
21. Bjerrum, N. *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **7** (1926) No. 9.
22. Davies, C. W. *Trans. Faraday Soc.* **23** (1927) 354.
23. Kenttämaa, J. *Acta Chem. Scand.* **12** (1958) 1323.
24. Seidell, A. *Solubilities of Inorganic and Metal-organic Compounds*, 3rd Ed. Vol. 1, D. Van Nostrand, New York 1940.
25. Muller, J.-A. *Bull. soc. chim. France* **23** (1918) 13.
26. Rossini, F. D., Wagman, D. D., Ewans, W. H., Levine, S. and Jaffe, I. *Selected Values of Chemical Thermodynamical Properties*, Natl. Bur. Standards (U.S.) Circ. No. 500 Washington 1952, p. 419.
27. Volmer, M. and Weber, A. *Z. physik. Chem.* **119** (1926) 277.
28. Volmer, M. *Kinetik der Phasenbildung*, Steinkopff, Dresden and Leipzig 1939.
29. Farkas, L. *Z. physik. Chem.* **125** (1927) 236.
30. Kaischew, R. and Stranski, I. N. *Z. physik. Chem.* **B26** (1934) 317.
31. Becker, R. and Döring, W. *Ann. Physik* **24** (1935) 719.
32. Cabrera, N. and Burton, W. K. *Discussions Faraday Soc.* **5** (1949) 40.
33. Burton, W. K., Cabrera, N. and Frank, F. C. *Trans. Roy. Soc. London,* Ser. A **243** (1951) 299.
34. Frank, F. C. *Discussions Faraday Soc.* **5** (1949) 48.
35. Born, M. and Stern, O. *Sitz.-ber. preuss. Akad. Wiss. Physik. math. Kl.* **1919** 901, p. 908.
36. Bruzs, B. *J. Phys. Chem.* **34** (1930) 621.
37. Hulett, G. A. *Z. physik. Chem.* **37** (1901) 385.
38. Dundon, M. L. *J. Am. Chem. Soc.* **45** (1923) 2658.
39. Freundlich, H. *Kapillarchemie*, Akademische Verlagsgesellschaft, Leipzig 1909, p. 145.
40. Freundlich, H. *Kapillarchemie*, 4th ed. Akademische Verlagsgesellschaft, Leipzig 1930, Vol. 1, p. 220.
41. Cohen, E. and Blekkingh Jr., J. J. A. *Koninkl. Ned. Akad. Wetenschap. Proc.* **43** (1940) 32, 189, 334.