# Some Variables Affecting the Rate of Crystal Growth in Aqueous Solutions

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A large amount of work, both theoretical and experimental, has been done on studies of crystal form and crystallography, the structure of crystals, crystal habits, and some phases of crystal growth and dissolution. However, relatively few researches have been reported which furnish equations relating the various variables affecting growth such as the specific crystallization velocity coefficient, rate of growth, supersaturation, and temperature or which furnish equations which are useful for the practical design of industrial crystallizers.

The theoretical work of Volmer, Stanski, Becker, and others (*1*) has provided a semiquantitative basis for understanding the factors that control the rate of nucleation and growth. Miers and his co-workers (*2*), following an earlier suggestion by Ostwald, postulated the existance of a supersolubility curve approximately parallel to the usual saturation curve dividing the supersaturated region into a metastable (low supersaturation) region and a labile (high supersaturation) region. In accordance with Miers' theory crystal growth occurs in both regions, while nucleation can occur only in the labile region.

Modern diffusion theories may be said to date from the publication of a work, dealing principally with the dissolution of crystals, by Noyes and Whitney (*3*) in 1897. For the rate of solution they proposed the equation

$$\frac{dw}{d\theta} = k_d a \, (C_s - C) \tag{1}$$

Weyberg (*4*) in 1901 studied crystal growth and showed that the various crystal faces grow at different rates.

In 1904 Nernst (*5*) studied solution velocities and modified the Noyes and Whitney equation by defining the constant of the equation as $k_d = D/\delta$. Nernst concluded that in dissolution, diffusion is entirely controlling and that by intense agitation the film thickness can be made to assume very small values. In applications to crystal growth he also found the diffusion gradient to be equal to the degree of supersaturation.

Berthoud (*6*) was the first to investigate crystal growth on the basis that there is not, as assumed in the pure diffusion theories, an infinitely rapid reaction at the crystal surface. He postulated a theory on the assumptions that the diffusional process is followed in series by a first-order interfacial reaction, the net rate of crystallization depends on both the rate of diffusion and on the rate of interfacial reaction, and the concentration of solution at the crystal surface is not, as assumed by Nernst, the saturation concentration but some higher value which is less than the supersaturation concentration in the bulk of the solution. He proposed for the diffusion process the equation

$$\frac{dw}{d\theta} = \frac{Da}{\delta} (C - C_i) \tag{2}$$

and for the interfacial reaction process the equation

$$\frac{dw}{d\theta} = k \, a \, (C_i - C_s) \tag{3}$$

A combination of these two equations and the elimination of $C_i$, a quantity which cannot be measured directly, results in the

$$\frac{dw}{d\theta} = \frac{a \, (C - C_s)}{\dfrac{1}{k} + \dfrac{\delta}{D}} \tag{4}$$

This equation, first derived by Berthoud, is essentially the same as that obtained by Valeton (*7, 8*) and by Friedel (*9, 10*). This theory has become known as the *Berthoud-Valeton theory*.

McCabe (*11*) from theoretical considerations derived the equation

$$\frac{dL}{d\theta} = K' f \, (C - C_s) \tag{5}$$

This equation is the basis of the $\Delta L$ law which McCabe postulated. In accordance with this law all geometrically similar crystals of the same material suspended in the same solution grow at the same rate, if the growth is measured as the increase in length of geometrically corresponding distances on all of the crystals.

It should be pointed out that the diffusional resistance $R_d$ in Equation (7) is affected by crystal size. If the external diffusion is appreciable in comparison with overall conductance, and if the velocity of the crystals through the mother liquor is constant, there should be a small effect on particle size. However this effect is small and becomes lost in actual experiments.

## THEORY

In order to clearly present the work accomplished and the conclusions therefrom obtained as a result of this in-

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vestigation it is necessary to review the theoretical development.

The basic law of any rate process may be written in the form of the general rate equation

$$\text{rate} = \frac{\text{driving force}}{\text{resistance}} \tag{6}$$

In chemical engineering, as is well known, this equation is applied to various phenomena of unit operations where the rates of mass or energy transfer are involved.

Crystallization combines two consecutive rate processes, the first consisting of diffusion of the solute through a stagnant film at the crystal surface, and the second consisting of the integration or mass transfer of the solute from the solution into the solid crystal surface. If it is assumed that the integration of solute into the solid crystal surface is a first-order reaction, then the two consecutive rate processes may be mathematically expressed as Equations (2) and (3), respectively. During steady state crystallization or growth the diffusion rate must equal the integration rate, so that Equations (2) and (3) may be combined to eliminate $C_i$, the concentration at the interface, and written in the from of Equation (5), the Berthoud-Valeton equation.

Examining this equation one sees that the equation may be rewritten in the form of Equation (6) as

$$\frac{dw}{d\theta} = \frac{a(C - C_s)}{R_i + R_d} \tag{7}$$

When the diffusional resistance is very large as compared with the integration resistance, $1/k$ becomes negligible, the equation reduces to the diffusion process Equation (2), as put forth by Berthoud, and diffusion becomes rate controlling. Likewise when the integrational resistance is very large, $\delta/D$ becomes negligible, the equation reduces to the integration process Equation (3), and integration or mass transfer of the solute into the solid surface becomes rate controlling.

In any case the equation may be written as

$$\frac{dw}{d\theta} = k' \, a \, (C - C_s) \tag{8}$$

If a single crystal having $n$ faces is considered, the rates of growth of each of the various faces may be expressed by the following series of equations:

$$\begin{aligned} \frac{dw_1}{d\theta} &= k'_1 \, s_1 \, a \, (C - C'_{s1}) \\ \frac{dw_2}{d\theta} &= k'_2 \, s_2 \, a \, (C - C'_{s2}) \\ &\vdots \\ \frac{dw_n}{d\theta} &= k'_n \, s_n \, a \, (C - C'_{sn}) \end{aligned} \tag{9}$$

where

$$a_1 = s_1 a, \; a_2 = s_2 a \; \ldots . \; a_n = s_n a, \tag{10}$$

for each of the faces, respectively.

Combining the series of Equations (9) and writing in summation form one obtains

$$\sum_{1\ldots n} \frac{dw}{d\theta} = aC \sum_{1\ldots n} k'_s - a \sum_{1\ldots n} k'_s \, C'_s \tag{11}$$

Since each of the faces of a crystal grow at a different velocity, the temperature of the interface must necessarily vary from face to face. Therefore the saturation concentration also must vary from face to face. However for relatively low supersaturations the interface temperature of each of the faces is nearly the same, and as an approximation an average saturation concentration may be used; therefore

$$\sum_{1\ldots n} k' \, s \, C'_s = C'_{s\,\text{avg}} \sum_{1\ldots n} k' \, s \tag{12}$$

For exothermic integration of solute into the interface the average saturation concentration $C'_s$ of each of the various crystal faces is greater than the saturation concentration corresponding to the saturation temperature of the bulk solution. One may write

$$\frac{C'_{s\,\text{avg}}}{C_s} = k_c \tag{13}$$

Substituting Equations (12) and (13) in (11) one obtains

$$\sum_{1\ldots n} \frac{dw}{d\theta} = a \, (C - k_c \, C_s) \sum_{1\ldots n} k' \, s,$$

Since $k_c$ is approximately 1, therefore for a single crystal

$$\frac{dw_{\text{total}}}{d\theta} = K'' \, a \, (C - C_s) \tag{14}$$

The area and weight of a single crystal may be expressed by each of the following equations, respectively:

$$a = eL^2 \tag{15}$$

$$w = \rho b L^3 \tag{16}$$

For a group of $N$ crystals the average size is

$$\bar{L} = \frac{\Sigma L}{N} \tag{17}$$

The average area per crystal is

$$\bar{a} = \frac{e \Sigma L^2}{N} \tag{18}$$

while the size of the crystal of average area is

$$\bar{L_a} = \left[ \frac{\Sigma L^2}{N} \right]^{1/2} \tag{19}$$

The average weight per crystal is

$$\bar{w} = \frac{\rho b \Sigma L^3}{N} \tag{20}$$

while the size of the crystal of average weight is

$$\bar{L_w} = \left[ \frac{\Sigma L^3}{N} \right]^{1/3} \tag{21}$$

For a group of $N$ crystals of narrow size distribution one may write the approximation:

$$\bar{L} = \bar{L_a} = \bar{L_w} \tag{22}$$

On the basis of Equation (14) the rate of growth of a group of any number of crystals may be expressed in terms of the equation

$$\frac{dW}{d\theta} = K'' \, A \, \Delta C_s \tag{23}$$

The total weight of a group of $N$ crystals of narrow size distribution may be expressed as

$$W = N \, \rho \, b \, \bar{L}^3 \tag{24}$$

From the above equation, for the growth process it follows that

$$\frac{\Delta(W^{1/3})}{N^{1/3}} = (\rho b)^{1/3}\,\Delta L \tag{25}$$

Likewise for the total area of $N$ crystals of narrow size distribution one may write

$$A = N\,e\,\overline{L}^2 \tag{26}$$

Combining Equations (24) and (26) to eliminate $\overline{L}$ one may write

$$A = \frac{N^{1/3}\,e}{(\rho b)^{2/3}}\,W^{2/3} \tag{27}$$

Using the above expression to eliminate the total area from Equation ( 3) and then rearranging one obtains

$$\frac{1}{N^{1/3}}\,\frac{dW}{W^{2/3}} = \frac{eK''}{(\rho b)^{2/3}}\,\Delta C_s\,d\theta \tag{28}$$

Integrating between the limits of $W_1$ and $W_2$, the total weight of the group of crystals before and after growth, one obtains

$$\frac{W_2^{1/3} - W_1^{1/3}}{N^{1/3}} = \frac{e}{3(\rho b)^{2/3}}\int_0^\theta K''\,\Delta C_s\,d\theta$$

or incorporating the shape factors and the density into $K$, the specific crystallization or growth velocity coefficient, one obtains

$$\frac{W_2^{1/3} - W_1^{1/3}}{N^{1/3}} = \int_0^\theta K\,\Delta C_s\,d\theta \tag{29}$$

where

$$K = \frac{e}{3(\rho b)^{2/3}}\,\frac{C'_{s\,\mathrm{avg}}}{C_s}\sum\frac{s}{\dfrac{1}{k}+\dfrac{s}{D}}$$

Equation (29) is a general equation which governs the growth of crystals in supersaturated solutions.

If the growth of crystals were carried out isothermally, then values of the specific growth velocity coefficient $K$ may be determined from experiment by measurements of the initial and final weights, the crystal count, and the supersaturation as a function of time from the expression

$$K = \frac{\dfrac{\Delta(W^{1/3})}{N^{1/3}}}{\displaystyle\int_0^\theta \Delta C_s\,d\theta} \tag{30}$$

The above equation is based on the assumption that for isothermal growth the specific growth velocity coefficient is independent of supersaturation.

## EXPERIMENT

The study (*12*) was made on the growth of potassium alum crystals in a laboratory batch crystallizer. Potassium alum was chosen for this study because of the ability to attain relatively stable highly supersaturated solutions.

The main components of the crystallizer unit were a stainless steel crystallizer drum and tank, the thermostatic bath, and the thermostatic control system. The crystallizer drum was of stainless steel construction, cylindrical in shape, 15 in. in diameter and length. The circumferential surface of the drum was perforated with ⅛-in. holes drilled on ½-in. centers. Six paddles 2 in. wide were bolted longitudinally at equal intervals perpendicular to and on the circumferential exterior surface of the drum. During operation the paddles provided agitation, forcing the liquid through the holes and over the surfaces of the crystals inside the drum. A constant agitation rate was used, and all growth runs were made at a drum speed of 1 rev./min. The drum was suspended in a semi-cylindrical stainless steel crystallizer tank. A cover was provided to fit over the drum and tank to prevent contamination of the solution by impurities and to minimize solvent loss by evaporation.

The crystallizer tank was suspended in a thermostatic bath which was maintained at a controlled temperature. The bath was equipped with a water circulating pump, a heat exchanger for make-up heat, and a thermostatic control system. The thermostat consisted of a stainless steel coil containing approximately 5 lb. of mercury. The coil was connected to a glass capillary containing the electrical contact which relayed a signal to the heat exchanger steam inlet valve. A temperature change of 2.0°C. produced a change of 1 in. in the height of mercury column in the capillary.

Most of the runs were carried out isothermally. However in the experimental runs carried out at a constant rate of temperature drop a clock motor and pulley mechanism was used to lower the thermostatic set point at a constant rate, different sized pulleys being used for the different rates of cooling.

A number of isothermal runs were made. The specific crystallization velocity coefficient was determined from Equation (30), determining the crystal count, initial and final weight of the crystal group, and experimentally determining the supersaturation as a function of time. The value of $\int_0^\theta \Delta C_s d\theta$ was determined by graphical integration.

The crystallization solution was made with distilled water and a photographic grade of hydrated potassium alum. Although it was considered that a purer grade of alum might have been more satisfactory from the standpoint of retarding the effects of impurities on the rates of growth, based on the consideration of the large amounts of alum required to operate the crystallizer unit, it was decided that the photographic grade would be satisfactory. The saturated solution was made at a temperature of about 10°C. higher than the temperature at which the run was to be made. The solution was then supersaturated by cooling to the desired temperature. Previously counted and weighed crystal groups were placed into the crystal drum, the cover was set in place, and the motor was started. Hydrometer temperature readings and time were recorded at 15-min. intervals. The run was continued until the hydrometer readings became constant, indicating that saturation had been attained. The crystals were then removed from the drum, washed in alcohol, air dried, and then counted and weighed.

In general the method used in this investigation for determining the supersaturation involved the following:

1. Determination of the saturation concentration by temperature measurement and reading the saturation concentration from the solubility curve.
2. Measurement of the solution density with specially calibrated hydrometers.
3. At the measured density and temperature the saturation temperature of the solution was obtained from a temperature-density diagram plotted as constant concentration parameters in the supersaturated region. The solution concentration corresponding to the saturation temperature thus obtained was read from the solubility curve.
4. The supersaturation was obtained by difference of the solution concentration determined in (3) above and the saturation concentration from (1) above.

In order to accurately determine the density a special set of three hydrometers constructed by Rossello and Grove (*13*) which had a sensitivity of 0.007 gravity units/in. of stem emergence was used.

The solubility curve for potassium alum was obtained by a least-squares fit with solubility data from the literature (*14, 15*). The density-temperature saturation curve shown in Figure 3 was likewise obtained by means of a least-square fit of data obtained from the literature (*16, 17*). The constant concentration lines shown in Figure 1 were determined for nine solutions of various concentrations and correlating the slopes, the change in temperature with density, with the saturation temperature by means of a least-square fit.

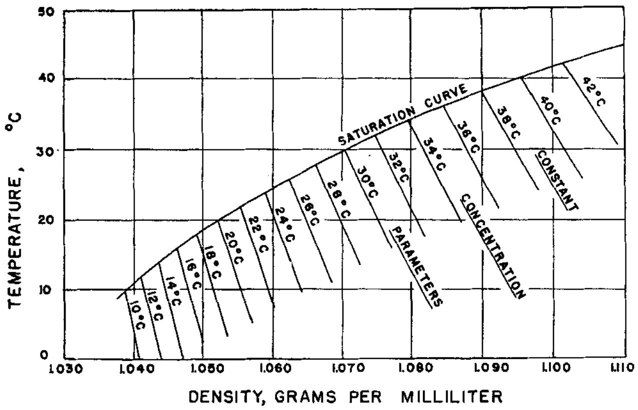

Fig. 1. Temperature-density diagram of potassium alum solutions.

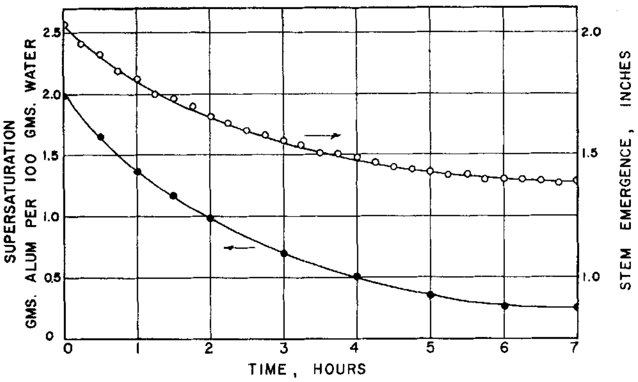

Fig. 2. Stem emergence and supersaturation vs. time for isothermal run number 3.

## ISOTHERMAL GROWTH

The specific crystallization rate coefficient was determined for the isothermal runs by means of Equation (30) which is based on the assumption that the coefficient is independent of supersaturation. A series of ten runs was made isothermally at low supersaturations, the average supersaturation for this group of runs ranged from approximately 0.42 to 0.80 g./100 g. of water. Typical plots of hydrometer stem emergence vs. time and supersaturation vs. time are shown in Figure 2.

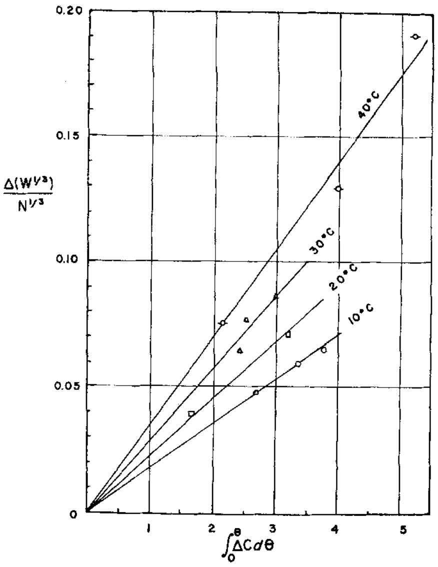

Fig. 3. Plot of $\Delta(W^{1/3})/N^{1/3}$ vs. $\int_0^\theta \Delta C d\theta$.

By graphical integration of the supersaturation vs. time curve the $\int_0^\theta \Delta C_s d\theta$ was determined, and the value of $\frac{\Delta(W^{1/3})}{N^{1/3}}$ was calculated from the crystal count and the initial and final weights of crystal groups. The results obtained are tabulated in Table 1. A plot of these results for the isothermal runs made at 10°, 20°, 30°, and 40°C. is shown in Figure 3. The slope of the lines obtained is the specific crystallization rate coefficient of Equation (30), and it is seen from the plot that the specific rate coefficient increases with increasing temperature.

With a least-square fit it was found that

$$K = 0.000546\,t + 0.0125 \tag{31}$$

Table 1. Summary of Results of Isothermal Crystal Growth Runs

| Run no. | $t$, °C. | $\theta$, hr. | Group | $\frac{\Delta(W^{1/3})}{N^{1/3}}$ | $\int_0^\theta \Delta C d\theta$ | $\Delta C_s$, avg. | Growth rate coefficient, $K$ |
|---|---|---|---|---|---|---|---|
| 5 | 9.7 | 8.0 | — | 0.0597 | 3.39 | 0.424 | 0.0176 |
| 6 | 9.7 | 8.0 | — | 0.0660 | 3.79 | 0.474 | 0.0174 |
| 7 | 9.7 | 5.50 | A | 0.0499 | 2.69 | 0.489 | 0.0186 |
| | | | B | 0.0495 | | | 0.0184 |
| | | | C | 0.0468 | | | 0.0174 |
| 16 | 20.0 | 7.0 | A | 0.0706 | 3.20 | 0.457 | 0.0221 |
| | | | B | 0.0714 | | | 0.0224 |
| | | | C | 0.0713 | | | 0.0224 |
| 17 | 20.0 | 4.25 | A | 0.0398 | 1.68 | 0.395 | 0.0237 |
| | | | B | 0.0394 | | | 0.0234 |
| | | | C | 0.0397 | | | 0.0238 |
| 12 | 30.0 | 5.0 | A | 0.0865 | 2.98 | 0.593 | 0.0290 |
| | | | B | 0.0863 | | | 0.0290 |
| 13 | 30.0 | 4.25 | A | 0.0666 | 2.43 | 0.572 | 0.0275 |
| | | | B | 0.0651 | | | 0.0268 |
| | | | C | 0.0633 | | | 0.0260 |
| 14 | 30.0 | 6.0 | A | 0.0793 | 2.52 | 0.420 | 0.0315 |
| | | | B | 0.0755 | | | 0.0300 |
| 1 | 40.0 | 5.0 | — | 0.1298 | 3.99 | 0.800 | 0.0325 |
| 2 | 40.0 | 3.0 | — | 0.0756 | 2.14 | 0.713 | 0.0353 |
| 3 | 40.0 | 7.0 | — | 0.1910 | 5.24 | 0.749 | 0.0365 |

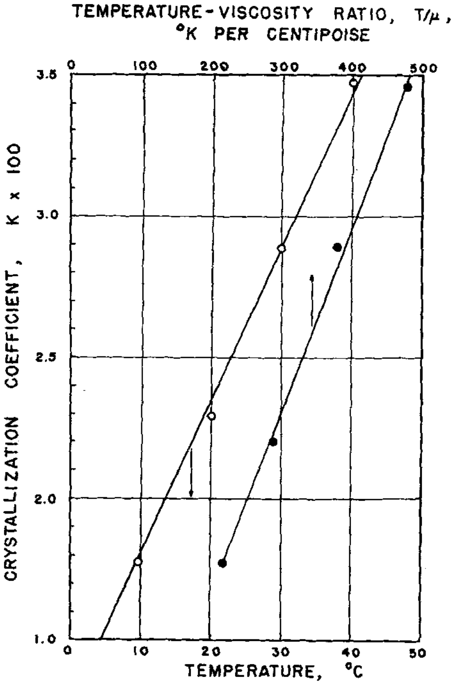

**Fig. 4. Crystallization coefficient vs. temperature and the temperature-viscosity ratio of water.**

A plot of $K$ vs. temperature is shown in Figure 4.

In accordance with Glasstone, Laidler, and Eyring (*18*) it is indicated that the effect of temperature on the diffusion coefficient $D$ for a solute in solutions may be estimated by assuming that $D\mu/T$ is independent of temperature, where $\mu$ is the viscosity of the solution and $T$ is the absolute temperature. It is well to note also that the diffusion coefficient varies not only with temperature but also with concentration, especially if the solution is nonideal. Because of the lack of data on viscosity of saturated potassium alum solutions a plot of the crystallization coefficient vs. the temperature-viscosity ratio of water was made. This is also shown in Figure 4. Previously it was shown that the specific crystallization rate coefficient $K$ is inversely proportional to the sum of the diffusional and integrational resistances. Since $K$ is directly proportional to $T/\mu$, and $D\mu/T$ is essentially constant for solutions, it may be concluded that the diffusional process was rate controlling in the isothermal runs which the data represent.

## CRYSTAL GROWTH AT CONSTANT RATE OF COOLING

A series of growth runs was made in which the solution was cooled at a constant rate. These runs were carried out in order to confirm the $K$ values determined during the isothermal growth runs. This was done by applying the general growth rate Equation (29) with values of $K$ which varied with temperature in accordance with the experimentally determined Equation (31). The method of calculation was similar to that used in the isothermal runs except that $K$ was determined at point conditions from Equation (31).

The values of $\frac{\Delta(W^{1/3})}{N^{1/3}}$ were calculated as before, and the values of $\int_o^\theta K\,\Delta C_s d\theta$ were determined by graphical integration of a plot of $K\,\Delta C_s$ vs. $\theta$. The results are tabulated in Table 2. It was found that the agreement between $\frac{\Delta(W^{1/3})}{N^{1/3}}$ and the $\int_o^\theta K\,\Delta C d\theta$, depended largely on supersaturation.

In the runs (numbers 28, 29, and 30) made at a low average supersaturations good agreement was obtained, except in run number 29 during which partial plugging of the perforations in the crystal drum occurred. During these runs the average supersaturation was approximately 0.60 as compared with supersaturations ranging from 0.42 to 0.80 during the isothermal runs used to determine the $K$ values. A comparison of runs numbers 23, 27, 18, and 20 made at higher supersaturations reveals an increasing deviation between $\int_o^\theta K\,\Delta C d\theta$ and $\frac{\Delta(W^{1/3})}{N^{1/3}}$ as the supersaturation increases. A comparison of all of these runs shows, in Table 2, that as the supersaturation increases from 0.60 to 4.14 the ratio of $\int_o^\theta K\,\Delta C d\theta / \frac{\Delta(W^{1/3})}{N^{1/3}}$ increases from 1.01 to 9.99. This indicates that the actual values of $K$ decrease with supersaturation, as would be expected on the basis that diffusion is rate controlling at low supersaturations and integration becomes rate controlling at high supersaturations. A plot of this ratio vs. the average supersaturation is shown in Figure 5.

## CONFIRMATION OF THE McCABE ΔL LAW

A quantitative confirmation was made during several of the isothermal runs of the McCabe $\Delta L$ law by calculating $\frac{\Delta(W^{1/3})}{N^{1/3}}$ for each of the different size groups of crystals grown during the same run under identical conditions. Since in accordance with Equation (25) $\frac{\Delta(W^{1/3})}{N^{1/3}}$ is directly proportional to $\Delta L$, and since it may be seen in the results tabulated in Table 3* that the agreement in

TABLE 2. SUMMARY OF RESULTS OF CRYSTAL GROWTH RUNS MADE AT CONSTANT COOLING RATE

| Run no. | $t_1$, °C. | $t_2$, °C. | $\theta$, hr. | Cooling rate, °C./hr. | $\Delta C_1$ | $\Delta C_2$ | $\Delta C_s$, avg. | $\frac{\Delta(W^{1/3})}{N^{1/3}}$ | $\int_o^\theta K\,\Delta C d\theta$ | $\frac{\int_o^\theta K\,\Delta C d\Delta\theta}{\Delta(W)^{1/3}/N^{1/3}}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 28 | 38.0 | 23.4 | 24 | 0.61 | 0.60 | 0.61 | 0.60 | 0.427 | 0.432 | 1.012 |
| 29 | 38.0 | 18.2 | 20.5 | 0.97 | 1.00 | 0.42 | 0.60 | 0.246 | 0.346 | 1.407 |
| 30 | 34.0 | 17.4 | 9.0 | 1.84 | 1.12 | 0.68 | 0.59 | 0.125 | 0.129 | 1.032 |
| 23 | 38.7 | 33.6 | 6.0 | 0.85 | 2.99 | 1.10 | 1.59 | 0.099 | 0.297 | 3.000 |
| 27 | 38.7 | 29.5 | 5.5 | 1.67 | 3.90 | 2.08 | 2.60 | 0.1054 | 0.461 | 4.374 |
| 18 | 40.8 | 37.1 | 10.25 | 0.36 | 4.30 | 2.64 | 3.00 | 0.1764 | 1.01 | 5.726 |
| 20 | 40.8 | 37.0 | 6.25 | 0.59 | 3.60 | 4.17 | 4.14 | 0.0881 | 0.880 | 9.989 |

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* Tabular material has been deposited as document 7845 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or for 35-mm. microfilm.

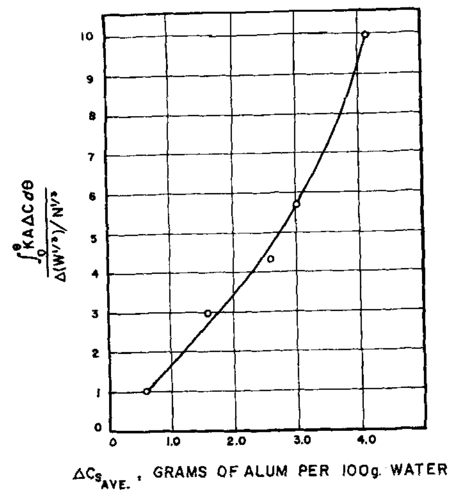

Fig. 5. $\frac{\int_0^\theta KA\Delta Cd\,\theta}{\Delta(W^{1/3})/N^{1/3}}$ vs. supersaturation.

$\frac{\Delta(W^{1/3})}{N^{1/3}}$ for each of the groups in any of the runs is good, this is in direct substantiation of McCabe's $\Delta L$ law.

## CONCLUSIONS

1. A crystallization Equation (29) for the rate of growth of crystals has been developed and confirmed experimentally to hold for groups of crystals of uniform size in solutions having a low degree of supersaturation in the growth of potassium alum crystals.

2. Values of the specific crystallization rate coefficient have been determined for potassium alum crystals growing in aqueous solutions at several temperatures and have been found to be linear with temperature in accordance with Equation (31).

3. It has been shown that the change in size factor $\frac{\Delta(W^{1/3})}{N^{1/3}}$ for any group of crystals of uniform size is directly proportional to the change in crystal size $\Delta L$ in accordance with Equation (25).

4. It has been shown experimentally that the change in size factor for each size group of crystals grown under nearly identical conditions is essentially constant. This is in conformance with the McCabe $\Delta L$ law.

5. It has been established that at low degrees of supersaturation in the growth of potassium alum the diffusion process is rate controlling as substantiated by the linearity between the specific crystallization rate coefficient $K$ and the temperature-viscosity ratio of water.

6. At high degrees of supersaturation the integration process becomes rate controlling in the growth of potassium alum crystals as evidenced by the fact that as the supersaturation increases the ratio of $\int_0^\theta K\Delta C_s d\theta$ to $\frac{\Delta(W^{1/3})}{N^{1/3}}$ increases at an increasing rate, the ratio having been computed on the basis of values of $K$ determined at low supersaturations.

## NOTATION

$a$ = surface area of a single crystal
$\overline{a}$ = average area of a group of crystals
$A$ = total area of a group of crystals
$b$ = volume shape factor of a crystal
$C$ = concentration of the bulk solution
$C_s$ = saturation concentration of the bulk solution
$C'_s$ = saturation concentration of a crystal face
$C_i$ = concentration of the solution at the interface
$D$ = coefficient of diffusion
$e$ = area shape factor of a crystal
$k$ = specific integration velocity coefficient at the interface
$k'$ = $1/(R_i + R_d)$ = the reciprocal of the sum of the integrational and diffusional resistances
$k_d$ = constant
$K'$ = constant
$K''$ = $\sum_{1....n} k'S$
$K$ = specific growth velocity coefficient
$L$ = linear dimension of a crystal between any two specifically defined corners
$\overline{L}$ = average linear dimension of a group of crystals
$\Delta L$ = $\overline{L_2} - \overline{L_1}$ = the change in the average linear dimension of a group of crystals
$n$ = number of faces of a single crystal
$N$ = number of crystals
$R_i$ = $1/k$ = integration resistance
$R_d$ = $S/D$ = diffusional resistance
$s$ = fraction of the total surface area of a single crystal for a single face
$t$ = temperature, °C.
$T$ = absolute temperature, °K.
$w$ = weight of a single crystal
$\overline{w}$ = average weight of a group of crystals
$W$ = total weight of a group of crystals
$\frac{\Delta(W^{1/3})}{N^{1/3}}$ = change in average weight or size factor of a group of crystals
$\Delta C_s$ = $C_s - C$, the supersaturation
$\delta$ = thickness of the diffusion film
$\rho$ = density
$\mu$ = viscosity
$\theta$ = time

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