

## COMPARISON OF COPPER SULPHATE PENTAHYDRATE GROWTH RATES DETERMINED BY DIFFERENT METHODS

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Crystal growth rates of copper sulphate pentahydrate ( $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ ) determined by different authors and methods are compared. The methods included in this comparison are: (i) Measurement on a fixed crystal suspended in a streaming solution, (ii) measurement on a rotating disc, (iii) measurement in a fluidized bed, (iv) measurement in an agitated suspension. The comparison involves critical estimation of the supersaturation used in measurements, of shape factors used for data treatment and a correction for the effect of temperature. Conclusions are drawn for the choice of values to be specified when data of crystal growth rate measurements are published.

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Methods for crystal growth rate measurements can be divided into direct and indirect methods<sup>1</sup>. In the direct methods, the movement of a chosen crystal face in its perpendicular direction, or the mass increase of a single crystal or of a number of crystals of equal size is determined. This group involves, in particular, the measurement of growth of a single crystal fixed on a holder in a streaming supersaturated solution, the measurement of growth of crystals in a fluidized bed and the measurement on a rotating disc. The indirect growth rate measurements can employ, e.g., the evaluation of the crystal size distribution of products from a continuous or batch crystallizer; in a closed quasiisothermal system, the growth rate of crystals can be determined also from the measurement of the desupersaturation rate or by using thermometric measurements.

Copper sulphate pentahydrate,  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ , belongs to the substances whose growth rate from aqueous solutions has been measured by several authors using different methods. The aim of this paper is to compare different methods of measurement and to evaluate the consistency of measured values of copper sulphate, using the published data. In order to make such a comparison, it was necessary to convert the results by different authors to the recommended units: in most cases, this procedure represented a new treatment of primary experimental data (where they had been published with necessary specifications), and their uniform representation as the dependence of the mean mass growth rate on the supersaturation at constant tempe-

perature and constant slip velocity. In some cases, it was also necessary to estimate the shape factors not given by the authors.

This paper does not comprise methods based on the solution of the population balance of a crystallizer: here, the determination of the crystal growth rate is also possible but the simultaneous determination of the corresponding supersaturation is absent in most cases so that no comparison with other data given in this paper can be made. In addition, the determination of the crystal size distribution is complicated by growth dispersion, which causes the apparent crystal size dependence of calculated growth rates<sup>2</sup>.

### THEORETICAL

The crystal growth rate is usually represented in the form of a dependence of the mean mass growth rate  $\dot{m}_A$  (defined by the relationship

$$\dot{m}_A = dm_c / (A_c dt), \quad (1)$$

where  $t$  is the time,  $m_c$  is the mass of a crystal and  $A_c$  its surface area) on the supersaturation of solution  $\Delta w$ , expressed as the difference between the actual concentration of solution  $w$  (in kg of hydrate/kg of free water) and the corresponding equilibrium concentration  $w_{eq}$  at a given temperature

$$\Delta w = w - w_{eq}. \quad (2)$$

The dependence of the mean mass crystal growth rate  $\dot{m}_A$  on the supersaturation  $\Delta w$  is frequently expressed as an empirical power law

$$\dot{m}_A = k_G \Delta w^g. \quad (3)$$

The growth rate may also be expressed as a change of the characteristic crystal dimension  $L$  with time:

$$\dot{L} = dL/dt. \quad (4)$$

As the characteristic crystal dimension  $L$  one can choose the sieve diameter (i.e. the smallest aperture of a sieve through which the crystal can pass), or any crystallographic dimension; e.g., in measurements of the growth rate of an individual chosen crystal face the characteristic dimension is the perpendicular distance between the face and an opposite parallel plane. If the crystal is growing without changing its shape, i.e. geometrical similarity is retained during the growth, the relation between the mass growth rate and the linear crystallization rate is<sup>3</sup>

$$\dot{m}_A = (3\alpha Q_c / \beta) \dot{L} \quad (5)$$

and

$$\dot{L} = k'_G \Delta w^g, \quad (6)$$

where

$$k'_G = (\beta/3\alpha q_c) k_G. \quad (7)$$

Here,  $\alpha$  and  $\beta$  are the volume and surface shape factors, respectively (the volume of a crystal with a characteristic dimension  $L$  is  $V = \alpha L^3$ , its surface area is  $A = \beta L^2$ ).

Crystal growth rates are often treated using the model of diffusion layer which presumes that the crystallization process proceeds in two subsequent steps, the transport of the matter through a diffusion layer followed by the surface reaction – incorporation of the particles into the crystal lattice. In the steady state,

$$\dot{m}_A = k_d(w - w_i) \quad (8)$$

and

$$\dot{m}_A = k_r(w_i - w_{cq})^r, \quad (9)$$

where  $w_i$  is the solution concentration at the solid–liquid interface. Usually, the value  $r = 2$  is taken in the kinetic equation of the surface reaction, Eq. (9).

## LITERATURE DATA

### *Measurements on a Fixed Crystal in a Streaming Solution*

Hixson and Knox<sup>4</sup> determined the rate of mass change of a single crystal fixed on a wire holder in a flowing supersaturated solution and growing for a given time interval. Their experimental conditions are given in Table I. The surface area of the crystal was determined before the experiment. The diameter of a sphere having the same surface area has been chosen as the characteristic dimension of the crystal. The results of their measurements were correlated using equations similar to Eqs (8) and (9) with concentrations expressed in terms of the mole fractions,  $y$ , of the  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  hydrate in solution:

$$\dot{m}_A = M_{\text{hyd}} K_d \ln [(1 - y_i)/(1 - y)] \quad (10)$$

$$\dot{m}_A = M_{\text{hyd}} K_r (y_i - y_{cq})^2, \quad (11)$$

where  $M_{\text{hyd}} = 0.24968 \text{ kg mol}^{-1}$  is the molar mass of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ . For the coefficient  $K_d$  in the range of experimental conditions we have the relation of dimensionless variables<sup>4</sup>

$$K_d d_c / D_y = 0.29 (d_c v / \nu)^{0.6} (\nu / M_m D_y)^{0.3}, \quad (12)$$

where  $v$  is the flow rate of solution (ratio of the volume flow rate and the free cross-sectional area in the region of the crystal),  $\nu$  is the kinematic viscosity of the solution,  $M_m = yM_{\text{hyd}} + (1 - y)M_{\text{H}_2\text{O}}$  is the mean molar mass and  $D_y$  is the diffusion coefficient corresponding to Fick's law in the form  $\dot{m}_A = M_{\text{hyd}}D_y \text{grad } y$ . The diffusion coefficient  $D_y$  can be related to the usual diffusion coefficient  $D$  (corresponding to volume concentrations  $c$  in  $\text{mol m}^{-3}$ ) by

$$D_y = D \, dc/dy = D \varrho_1 M_{\text{H}_2\text{O}} [\varrho_1 - c(M_{\text{hyd}} - M_{\text{H}_2\text{O}})]^{-2}, \quad (13)$$

where  $M_{\text{H}_2\text{O}}$  is the molar mass of water and  $\varrho_1$  is the solution density.

The kinetic constant  $K_r$  in Eq. (11) has been expressed<sup>4</sup> in the form of an Arrhenius equation as

$$K_r = 6.812 \cdot 10^{11} \exp(-E_r/RT) \quad (14)$$

with  $E_r = 56.902 \text{ kJ mol}^{-1}$ .

From Eqs (10), (11), (12) and (14) the mean mass crystal growth rate  $\dot{m}_A$  for a required temperature can be calculated (i.e. with a known solubility  $w_{\text{eq}}$  and values of  $\nu$ ,  $D_y$ ,  $\varrho_1$  and  $M_m$  evaluated for the solution saturated at the given tempera-

TABLE I  
Survey of experimental conditions

Ref.	$T$ °C	$\Delta w$ $\text{kg kg}_0^{-1}$	Method	$L$ mm	$\nu$ $\text{cm s}^{-1}$	Shape factors
4	19.5–71.2	0.0061–0.0372	fixed cr. mass	8.6–18	2.4–112	yes
5	21.3	0.0426–0.0681	fixed cr. opt. (100)	ca 5	1.8–18.4	no
6	24.8–26	0.0352–0.0541	fixed cr. opt. (100)	3–10	0.9–8.6	yes
7	30	0.0002–0.0072	disc (110)	ca 7	2.5 rot $\text{s}^{-1}$	yes
8	27.8	0.01–0.042	fluid. bed	0.91–1.6	1.6–5.4	yes
9	27.1–30.1	0.007–0.042	fluid. bed	ca 1	4.1	yes
11	30	0.008–0.0414	fluid. bed	1–1.25	?	no
12	30	0.0013–0.0132	fluid. bed	0.6–0.75	5	ref. <sup>8</sup>
13	29.2–31.5	0.0092–0.033	fluid. bed	0.82–1.1	?	only $\alpha$
2	<28	0.0032–0.020	mixed susp.	0.3–0.5	?	—

ture) for a given flow rate  $v$  and a known equivalent crystal diameter  $d_e$ ; the value of the concentration  $y_i$  at the interface has been sought by iteration. The average deviation of experimental and calculated values was found to be 19%.

Using the equations above, we calculated the dependence of the growth rate  $\dot{m}_A$  on the supersaturation  $\Delta w$  at 30°C, flow rate  $v = 5 \text{ cm s}^{-1}$  and crystal size  $L = 1.5 \text{ mm}$ , because most of the other literature data refer to these conditions. The values of the properties of solution at 30°C were obtained by interpolation using the values for 19.3 and 41.4°C reported by Hixson and Knox<sup>4</sup>:  $v = 1.69 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$ ,  $\rho_1 = 1235 \text{ kg m}^{-3}$ ,  $D_y = 2.44 \cdot 10^{-5} \text{ mol m}^{-1} \text{ s}^{-1}$ . A plot of  $\dot{m}_A$  vs  $\Delta w$  for given conditions is shown in Fig. 1. In the experimental range of supersaturations this curve can be fitted to the empirical power law of Eq. (3) with the kinetic exponent  $g = 1.45$ . It is clear that the fit is adequate over a limited supersaturation range only. This is because Eqs (10) and (11) indicate that for small supersaturations ( $y - y_{eq}$ ), and hence for small values of  $(y_i - y_{eq})$ , the value of  $g$  approaches 2 and the governing process is the surface reaction, Eq. (11). For high supersaturations, on the other hand, the governing process is diffusion of the solute towards the crystal surface, Eq. (10), and the value of  $g$  will approach 1 because even for high supersaturations the value of  $y$  will not exceed 0.1 so that

$$\ln \left[ \frac{1 - y_{eq}}{1 - y} \right] \doteq y - y_{eq}.$$

Tai and Pan<sup>5</sup> measured the growth rate of the (100) face of a fixed copper sulphate crystal in a flow apparatus of a similar design as described by Hixson and Knox<sup>4</sup>. The chosen face (100) was perpendicular to the solution flow and its position as a function of time was monitored using a microscope. The measurement was performed at 21.3°C, and the authors investigated the effect of supersaturation and of

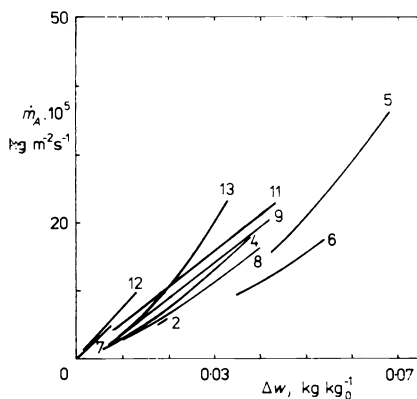


FIG. 1

Mean mass crystal growth rate of  $\text{CuSO}_4 \cdot 5 \text{ H}_2\text{O}$  as a function of supersaturation for temperatures close to 30°C and solution flow rates close to  $5 \text{ cm s}^{-1}$ ; experimental conditions given in Table I. The numbers correspond to individual references

flow rate on the growth rate of a crystal. The experimental conditions are summarized in Table I. As Hixson and Knox<sup>4</sup>, Tai and Pan<sup>5</sup> correlated the experimental data using the diffusion layer model. Thus we can write

$$l_{100} = k'_d(w - w_i) \quad (15)$$

$$l_{100} = k'_r(w_i - w_{eq})^2, \quad (16)$$

where  $l_{100}$  is the growth rate of the (100) crystal face (i.e. its velocity relative to the crystal center). The values of the constants  $k'_d$  and  $k'_r$  for various flow rates calculated from primary data reported by Tai and Pan<sup>5</sup> (where dimensionless concentrations  $w/w_{eq}$  are used) are summarized in Table II. The growth rate  $l_{100}$  can be obtained for a given supersaturation  $\Delta w = w - w_{eq}$  from Eqs (15) and (16) by elimination of the unknown concentration  $w_i$ :

$$l_{100} = k'_d[q - (q^2 - 1)^{1/2}] \Delta w \quad (17)$$

with

$$q = 1 + k'_d/(2k'_r \Delta w). \quad (18)$$

The shape factors, related to the characteristic dimension equal to the distance of two opposite parallel faces (100) and ( $\bar{1}00$ ) of the crystal of copper sulphate, were determined by König (see the next paragraph and Table IV). The growth rate of this characteristic dimension is equal to  $2 l_{100}$ . From Eq. (5) we obtain

$$\dot{m}_A = (6\alpha Q_c/\beta) l_{100} \quad (19)$$

TABLE II

Coefficients of the kinetic Eqs (15) and (16) calculated from data of Tai and Pan<sup>5</sup> for the growth rate of the (100) face of copper sulphate pentahydrate at 21.3°C in dependence on the flow velocity of the solution

$v$ cm s <sup>-1</sup>	$k'_d \cdot 10^5$	$k'_r \cdot 10^5$
1.80	0.629	1.59
2.78	0.681	1.77
5.15	0.785	1.93
11.01	0.857	2.07
13.95	0.904	2.10
18.4	1.030	2.11

and  $l_{100}$  for 21.3°C and  $v = 5.15 \text{ cm s}^{-1}$  is obtained from Eqs (17) and (18) by taking  $k'_d = 7.85 \cdot 10^{-6} \text{ m s}^{-1}$  and  $k'_r = 1.93 \cdot 10^{-5} \text{ m s}^{-1}$  from Table II. The values of  $\dot{m}_A$  obtained in this way for the experimental range of supersaturations<sup>5</sup> are plotted in Fig. 1.

König (not yet published data) measured the growth rate of the (100) crystal face of a copper sulphate crystal fixed in a circulating flow apparatus described in his thesis<sup>6</sup>. The growing face oriented perpendicularly to the solution flow was monitored using a microscope. The growth rate of the (100) face was investigated as a function of the supersaturation and the flow rate.

The values of shape factors  $\alpha$  and  $\beta$  related to the characteristic dimension equal to the distance between the two opposite faces (100) and ( $\bar{1}00$ ) were determined from measurements of relative crystal dimensions on photographs; the crystal shape was approximated by a rectangular prism. The measurement was carried out using a solution of constant concentration corresponding to saturation at 30°C; the super-

TABLE III  
Growth rate of the face (100) measured by König<sup>6</sup> in a circulating flow apparatus at 30°C

$T$ °C	$\Delta w$ kg kg <sub>0</sub> <sup>-1</sup>	$v$ cm s <sup>-1</sup>	$\dot{l}_{100} \cdot 10^8$ m s <sup>-1</sup>
26	0.0337	1.0	1.6
		1.0	1.3
		2.1	1.0
		4.7	2.0
		7.3	2.7
24.9	0.0425	0.9	2.4
		1.9	3.6
		1.3	3.5
		3.3	3.2
		8.6	3.3
24.8	0.0432	1.0	2.8
		2.0	1.8
		3.7	3.3
		4.2	1.4
		5.9	3.5
		8.0	2.7
23.85	0.0506	1.1	3.2
		3.3	3.7
		4.5	2.0
		7.8	3.0

saturation was produced by cooling down the solution. The experimental conditions and a survey of results of the kinetic measurements are summarized in Tables I and III, respectively. For each measurement a new crystal was used, so that the individual scatter of results probably overlaps the possible effect of flow rates of solution, as can be seen from Table III. This is why the growth rates of the (100) face as a function of supersaturation were evaluated all together independently of the flow rate, using the empirical power-law Eq. (6) in the form

$$l_{100} = k'_G \Delta w^g \quad (20)$$

with  $k'_G = 2.30 \cdot 10^{-6} \text{ m s}^{-1}$  and  $g = 1.46$ . Using the shape factors  $\alpha = 50.5$  and  $\beta = 131.4$ , we obtain from Eq. (19)

$$\dot{m}_A = 1.39 \cdot 10^{-2} \Delta w^{1.46}.$$

This dependence is depicted in Fig. 1.

#### *Measurements on a Rotating Disc*

Karel and Nývlt<sup>7</sup> measured the growth rate of the (1 $\bar{1}$ 0) face of a copper sulphate crystal by the method of rotating disc with a constant disc rotation speed of  $2.5 \text{ s}^{-1}$ . The growth rate of crystal face (1 $\bar{1}$ 0) is

$$l_{1\bar{1}0} = \Delta m_c / (A t_c), \quad (21)$$

where  $\Delta m_c$  is the mass increase in time  $t_c$  on the (1 $\bar{1}$ 0) face whose surface area is  $A$ . The mean mass growth rate  $\dot{m}_A$  can then be determined using an equation similar to Eq. (19)

$$\dot{m}_A = (6\alpha\beta/\beta) l_{1\bar{1}0}. \quad (22)$$

The shape factors  $\alpha$  and  $\beta$  in this equation are related to the characteristic dimension equal to the perpendicular distance between the opposite faces (1 $\bar{1}$ 0) and ( $\bar{1}$ 10). These shape factors were calculated from measurements on 15 crystals whose shape was approximated by a rectangular prism. The relationship between  $\dot{m}_A$  and the supersaturation at  $30^\circ\text{C}$  is given by Eq. (3) with  $k_G = 6.74 \cdot 10^{-3} \text{ kg m}^{-2} \text{ s}^{-1}$  and  $g = 1$ .

The dissolution rate of the (1 $\bar{1}$ 0) face at the same absolute value of the driving force  $\Delta w$  was 2.1 times higher than the rate of growth. In the same paper, measurement with a tablet pressed from crystals with sieve diameters in the range 0.1 to 0.2 mm is described. The results show that the growth rate of the tablet is by 20% higher than that of the slowest growing face (1 $\bar{1}$ 0). This means that the anisotropic



crystals of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  are not oriented on the tablet surface randomly but in such a way that the flat face  $(1\bar{1}0)$  prevails.

#### Measurements in a Fluidized Bed

In fluidized bed measurements, the mass increase of a number of seeds during their growth at constant supersaturation is the primarily measured value. Denoting the number of crystals by  $N_c$ , their initial and final mass by  $m_{c0}$  and  $m_{ce}$ , respectively, and the period of measurement by  $t_c$ , we can write

$$\dot{m}_A = [3(\alpha Q_c)^{2/3}/(\beta t_c N_c^{1/3})] (m_{ce}^{1/3} - m_{c0}^{1/3}). \quad (23)$$

In comparison with experimental kinetic data, the values of the shape factors  $\alpha$  and  $\beta$  are of great importance. These values for various characteristic dimensions of copper sulphate crystals are summarized in Table IV. While the values of  $\alpha$  and  $\beta$  and their ratio  $\beta/\alpha$  show a wide spread depending on the choice of the characteristic dimension (and probably also on the origin of crystals), the ratio  $\alpha^{2/3}/\beta$  appearing in Eq. (23) is relatively constant. This may indicate a certain stability in the shape of copper sulphate crystals used for measurements by various authors; the ratio  $\alpha^{2/3}/\beta = V^{2/3}/A$  is proportional to the sphericity  $\psi$  (i.e. the surface area of a sphere having the same volume as the crystal, divided by the crystal surface area):

$$\psi = (36\pi)^{1/3} \alpha^{2/3}/\beta. \quad (24)$$

TABLE IV  
Shape factors  $\alpha$  and  $\beta$  of the  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  crystals

Ref.	Shape approx. for calc. $\beta$	Charact. dimension	$\alpha$	$\beta$	$\beta/\alpha$	$\alpha^{2/3}/\beta$
9	slanted prism 2:20 : 1 : 0.777	(110) — ( $\bar{1}\bar{1}0$ )	0.13	1.59	12.2	0.133
		( $1\bar{1}0$ ) — ( $\bar{1}10$ )	1.42	7.70	5.42	0.135
		(11i) — $\bar{1}\bar{1}\bar{1}$	3.05	12.8	4.20	0.135
8	prism	sieve diam.	0.288	3.01	10.5	0.145
7	prism 1.50 : 1 : 0.356	( $1\bar{1}0$ ) — ( $\bar{1}10$ )	11.82	37.7	3.19	0.138
6	prism 2.10 : 1 : 0.204	(100) — ( $\bar{1}00$ )	50.5	131	2.60	0.104

It is therefore an advantage that the Eq. (23) for calculating the mean mass crystal growth rate in a fluidized bed contains shape factors just in the ratio  $\alpha^{2/3}/\beta$ .

The dependence of  $\beta$  on  $\alpha$  (for  $\alpha > 0.5$ ) can also be written as

$$\beta = 2.34 + 3.17\alpha - 0.012\alpha^2. \quad (25)$$

Karpiński<sup>8</sup> has used an apparatus with a packed section at the bottom of the measuring tube, which caused the velocity profile of solution to be flat. The mean mass crystal growth rate was determined as a function of supersaturation and kinetic coefficients  $k_d$  and  $k_r$  of individual steps appearing in Eqs (8) and (9) were calculated on the basis of the diffusion layer model. Five series of measurements were made with different flow rates of solution and seed sizes. The results are summarized in Table V. In Fig. 1, the results of series E are plotted with the flow rate (calculated for the free cross-sectional area of the tube)  $v = 5.54 \text{ cm s}^{-1}$  which is close to our value  $5 \text{ cm s}^{-1}$  chosen for comparison.

Matuchová<sup>9,10</sup> employed a fluidized-bed apparatus with a conical neck at the inlet. The flow rate in the middle part of the tube was  $v = 4.1 \text{ cm s}^{-1}$ . The crystals were periodically circulated between the upper and lower parts of the fluidized bed so that the flow could be characterized as a combination of the fluidization regime with axial mixing. Kinetic data<sup>9</sup> (after recalculation) represented as a plot of the linear coordinate  $l_{110}$  (calculated by Matuchová<sup>9</sup> from the overall growth rate) vs  $\Delta w$  give a straight line with a small positive intercept at the  $\Delta w$  axis

$$l_{110} = 4.65 \cdot 10^{-6} (\Delta w - 0.00271). \quad (26)$$

The mean mass growth rate is described by an equation analogous to Eq. (19)

$$\dot{m}_A = (6\alpha Q_c/\beta) l_{110} = 5.21 \cdot 10^{-3} (\Delta w - 0.00271), \quad (27)$$

TABLE V

Constants of kinetic Eqs (8) and (9) for the mean mass growth rate of  $\text{CuSO}_4 \cdot 5 \text{ H}_2\text{O}$  measured by Karpiński<sup>8</sup>

Series	$v$ $\text{cm s}^{-1}$	Sieve diam. mm	Porosity	$k_G \cdot 10^3$ Eq. (3)	$g$	$k_d \cdot 10^3$ Eq. (8)	$k_r$ Eq. (9)
A	1.64	1.24	0.589	6.18	1.21	5.59	0.52
B	2.64	0.905	0.771	12.4	1.44	6.23	0.28
C	2.64	1.25	0.803	11.5	1.44	5.14	0.32
D	4.07	1.27	0.872	13.9	1.41	6.50	0.48
E	5.54	1.64	0.942	10.3	1.30	7.05	0.53

where  $\alpha$  and  $\beta$  have the values given in Table IV. This dependence is depicted in Fig. 1.

Kočová and Nývlt<sup>11</sup> have given a survey of their growth rate data including also the growth rate of copper sulphate: for crystals of the size in the range 1.0–1.25 mm at 30°C, the values measured in a fluidized bed apparatus can be represented by Eq. (3) with  $k_G = 6.81 \cdot 10^{-3} \text{ kg m}^{-2} \text{ s}^{-1}$  and  $g = 1$ . In treating the experimental data using Eq. (23), they approximated the shape of crystals by a cube (shape factors  $\alpha = 1$  and  $\beta = 6$ ), i.e.  $\alpha^{2/3}/\beta = 0.167$ . Taking a more realistic value, given by Matuchová<sup>9</sup>,  $\alpha^{2/3}/\beta = 0.13$ , we obtain from Eq. (23) a new value of  $k_G$  which is lower by  $0.13/0.167 = 0.778$ . This new value,  $k_G = 5.30 \cdot 10^{-3} \text{ kg m}^{-2} \text{ s}^{-1}$  was used for the plot in Fig. 1.

Karel and Nývlt<sup>12</sup> measured the growth rate of  $\text{CuSO}_4 \cdot 5 \text{ H}_2\text{O}$  crystals in a fluidized bed apparatus with a neck similar to that used previously<sup>9–11</sup>. Modified sampling valves enabled the crystals to be introduced and withdrawn without interrupting the flow of solution so that the stability of temperature and hence the spread of measured values improved. The shape factors necessary for data treatment were taken from a paper of Karpiński<sup>8</sup>. For 30°C and a flow rate of  $5 \text{ cm s}^{-1}$ , the mean mass growth rate could be correlated by using Eq. (3) with  $k_G = (7.3 \pm 0.5) \cdot 10^{-3} \text{ kg m}^{-2} \text{ s}^{-1}$  and  $g = 1$ . This dependence is also depicted in Fig. 1.

Toyokura et al.<sup>13</sup> studied the secondary nucleation of copper sulphate in a fluidized bed and simultaneously also its growth rate. Their results are presented in the form of the growth rate of the sieve diameter on the supersaturation (kmole of anhydrous substance/kg  $\text{H}_2\text{O}$ ). They obtained the shape factor  $\alpha = 0.288$  which is identical with the value given by Karpiński<sup>8</sup>: this is why we applied the value of  $\beta$  given by Karpiński<sup>8</sup> for evaluation according to Eq. (5). The mass growth rate  $\dot{m}_A$  is then represented by Eq. (3) with parameters  $k_G = 5.21 \cdot 10^{-2}$  and  $g = 1.59$ . These results are also shown in Fig. 1.

#### *Growth in Agitated Suspension*

McCabe and Stevens<sup>2</sup> measured the growth rate of copper sulphate crystals in an agitated batch crystallizer by weighing the seeds and the product crystals. They used a starting temperature of 28°C, a mass concentration of the suspension of 0.5 g of crystals/1 000 g of solution, an agitation speed of 400 r.p.m. (the agitator is not specified) and a cooling rate of  $1.2 \text{ K h}^{-1}$ . During the run, the actual concentration of solution was monitored by conductometry. The authors made three series of experiments with crystals of narrow sieve fractions of 0.3, 0.4 and 0.5 mm. The increase in the size of crystals was determined by measurement of their length and width under a microscope, the characteristic dimension being defined as a geometric average of the width and length of crystals. Their initial size was determined by sieving, however. The size dependence of growth rate is probably not so dominant<sup>2</sup>.

In Table VI, the growth rate constants and the corresponding growth rate exponents  $g$  are given for given crystal sizes and supersaturations. It can be seen that the range of supersaturations (in particular for crystals of 0.4 and 0.5 mm in size) is very small so that the evaluation of the exponent  $g$  must be rather inaccurate. The shape factors used for evaluation were taken from a paper of Karpiński<sup>8</sup>.

## DISCUSSION

The growth rate of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  crystals has been measured in principle by five different methods: measurement of the mass increase of a single crystal fixed in a flowing solution; microscopic measurement of the growth rate of a chosen crystal face of a fixed single crystal in a flowing solution; measurement of the mass increase of a chosen crystal face or of a pressed tablet in a rotating disc; measurement of the mass increase of a number of crystals in a fluidized bed; and measurement of the growth of crystals in an agitated dilute suspension.

The main factor affecting the reliability of results is the accuracy in the determination of the supersaturation or the saturation concentration (or temperature) of the solution. The most inaccurate method is probably that consisting of weighing in the corresponding amount of solute calculated from solubility tables<sup>5</sup>; the error may arise from inaccuracy of tabulated data and from not exactly stoichiometric contents of water in the sample. It is, therefore, reasonable to control the supersaturation by visual observation of the corners and edges of a crystal suspended in the investigated solution using a microscope<sup>5</sup>. Perhaps more reliable should be thermostating the suspension of crystals for a sufficiently long period until it reaches the steady state<sup>4,6</sup>. A difficulty with measuring the saturation temperature of copper sulphate by this method is, however, that the equilibrium is reached extremely slowly so that even after several hours the solution can be still not completely saturated and thus the true supersaturation of such a solution may be less than the expected one. Conductometric determination of the supersaturation<sup>2</sup> is advantageous but it is necessary to control the temperature very carefully. The measurements have to be related to the

TABLE VI  
Crystal growth rate of copper sulphate according to McCabe and Stevens<sup>2</sup>

$L$ , mm	$\Delta w$	$k'_G \cdot 10^5$	$g$	$k_G$
0.3	0.0032—0.019	2.47	1.61	0.016
0.4	0.0137—0.0195	9.3	1.82	0.061
0.5	0.0177—0.0195	5.86	1.64	0.038

saturated solution, so the problem is again reduced to preparation of a saturated solution. The method of slow dissolution of the last tiny crystal<sup>9,11</sup> is, in general, very suitable for the determination of the saturation temperature; however, with copper sulphate exhibiting a very slow dissolution rate it is not sufficiently exact and may serve rather high supersaturation values: this may also be one of explanations of the intercept on  $\Delta w$  axis found by Matuchová<sup>9</sup> (another explanation is the curvature of the dependence in the range of small supersaturations according to the BCF theory). More reliable seems to be the extrapolation of mass increase of crystals or of the linear growth rate measured at different temperatures with the same solution to zero growth rate. Because this extrapolation in the region of small supersaturations need not be linear (curvature predicted by the BCF theory) and the growth may start only at a certain threshold supersaturation (e.g. in presence of growth inhibitors), it is recommended to check this value also by several experiments in the region of crystal dissolution.

Another parameter, also affecting the crystal growth rate, is the relative velocity between the crystal and the solution (slip velocity), in general the hydrodynamics of the system. This is well defined in the method of rotating disc<sup>7</sup>. For a fixed single crystal, the mass increase of the whole crystal<sup>4</sup> or the linear growth rate of a chosen crystal face<sup>5,6</sup> is measured; in the former case, the hydrodynamic conditions are different at different crystal faces so that the orientation of the single crystal is important and interpretation of the data may be difficult. In the latter case, the crystal orientation towards the streaming solution is also of importance but the orientation as well as the flow velocity are unambiguously determined. A more complex question is the definition of hydrodynamic conditions in a fluidized bed of crystals: a flat velocity profile in the whole tube cross section cannot be reached without special arrangement<sup>8</sup> and usually local turbulencies occur; crystals frequently circulate between the upper and the lower part of the fluidized bed<sup>9,12</sup>. The relative flow rate is characterized to some extent by the upflow velocity (calculated from the volumetric flow rate and the cross-sectional area of the tube, neglecting the volume of crystals)<sup>14</sup>, so that the true slip velocity is probably slightly higher than expected. It is of interest to note that in a properly operated fluidized bed, the mass transfer coefficient between a (spherical) particle and flowing solution is practically independent of the superficial velocity.

A complete survey of the dependence of mean mass growth rate on supersaturation at 30°C for crystals with the sieve diameter close to 1.5 mm and for the relative velocity crystal – solution close to 5 cm s<sup>-1</sup> is shown in Fig. 1. It is necessary to keep in mind that many measurements have been made at temperatures lower than the chosen temperature 30°C: Tai and Pan<sup>5</sup> measured at 21.3°C, König<sup>6</sup> at 24.8 to 26°C, Karpiński<sup>8</sup> at 27.8°C, Matuchová at 27.1–30.1°C. It follows from the work of Hixson and Knox<sup>4</sup> that the activation energy of the mass transport is about 21 kJ mole<sup>-1</sup> whereas that of the surface reaction (incorporation of particles into

the crystal lattice) is about  $56.9 \text{ kJ mole}^{-1}$ . Because the rate constants  $k_d$  and  $k_r$  in Eqs (8) and (9) are not known in many cases, we took conservatively for our temperature correction towards  $30^\circ\text{C}$  the activation energy of the mass transport, i.e.  $E = 21 \text{ kJ mole}^{-1}$  in all cases. The measured mass growth rates  $\dot{m}_A$  were then multiplied by an Arrhenius factor equal to  $\exp[(E/R) \cdot (1/T - 1/303.15)]$ , where  $R = 8.314 \text{ J mole}^{-1} \text{ K}^{-1}$  is the universal gas constant and  $T(\text{K})$  is the temperature of the measurement. The result is shown in Fig. 2. It is evident that the curves lie now closer together. Empirical constants  $k_G$  and  $g$  evaluated from Eq. (3) for indivi-

TABLE VII

Constants  $k_G$  and  $g$  from Eq. (3) describing the dependence of the mean mass growth rate on supersaturation calculated for the region of supersaturation listed in Table I

Ref.	$k_G$ $\text{kg m}^{-2} \text{ s}^{-1}$	$g$	$10^3 \cdot k_G^g$ $\text{kg}^g \text{ m}^{-2g} \text{ s}^{-g}$
4	0.0200	1.45	3.4
5	0.0592	1.81	6.0
6	0.0218	1.60	2.2
7	0.00674	1	6.7
8	0.0150	1.37	3.2
9	0.0113	1.24	3.8
11	0.0053	1	5.3
12	0.0073	1	7.3
13	0.0521	1.59	9.1
2	0.016	1.61	1.3

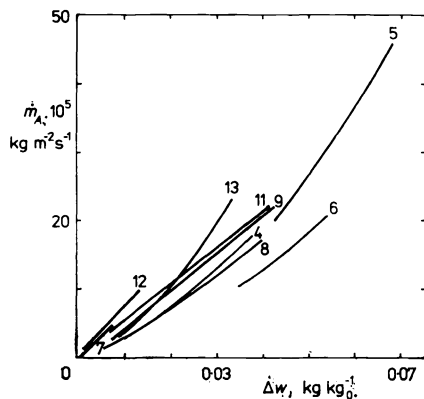


FIG. 2

Mean mass crystal growth rate of  $\text{CuSO}_4 \cdot 5 \text{ H}_2\text{O}$  as a function of supersaturation: data from Fig. 1 recalculated for the temperature  $30^\circ\text{C}$ . The numbers correspond to individual references

dual curves in the region of experimental values of the supersaturation are summarized in Table VII. As we mentioned already, this survey of kinetic data does not involve the results of crystallization measurements in dense agitated suspensions<sup>2</sup>.

It is evident from Table VII that the values obtained by various methods and presented by various authors differ in particular in the growth order  $g$  ranging from 1.0 (refs<sup>7,11,12</sup>) to 1.8 (ref.<sup>5</sup>). Low  $g$  values have been obtained in measurements in a dilute fluidized bed<sup>9,11,12</sup> whereas in a dense fluidized bed<sup>8</sup> (with voidage of about 0.8) and with a fixed single crystal<sup>4,5</sup>, the  $g$  values are higher. Measurement of the mass increase with rotating disc<sup>7</sup> gave a low value,  $g = 1$ ; relatively high values were obtained in optical measurement of the linear growth rate of an individual crystal face<sup>5,6</sup>. The values of  $k_G$  and  $g$  are not independent and can be correlated by

$$k_G = 0.094 - 0.17g + 0.085g^2 \quad (26)$$

or simply

$$k_G^g = 0.005 \quad (27)$$

(see Table VII).

The following conclusions have been drawn from the analysis of published papers dealing with crystal growth rate of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ : a) Care must be given to the determination of the supersaturation of the solution. As the supersaturation can be expressed easily by the undercooling below the saturation temperature, the problem reduces to the preparation of the saturated solution or to the exact determination of its saturation temperature. b) For further treatment of data, it is necessary to characterize thoroughly the shape of crystals used as seeds, and also to characterize any changes in crystal shape during the growth. c) Full effort must be made to characterize adequately the hydrodynamics of the system.

## SYMBOLS

( $\text{kg}_0$  means kg of free water)

$A$	surface area of crystal face, $\text{m}^2$
$A_c$	surface area of crystal, $\text{m}^2$
$c$	concentration, $\text{mole m}^{-3}$
$D$	diffusion coefficient, $\text{m}^2 \text{s}^{-1}$
$D_y$	diffusion coefficient, $\text{mole m}^{-1} \text{s}^{-1}$
$d_e$	equivalent crystal diameter, m
$E$	activation energy, $\text{J mole}^{-1}$
$E_d$	activation energy of mass transport step, $\text{J mole}^{-1}$
$E_r$	activation energy of surface reaction step, $\text{J mole}^{-1}$
$g$	kinetic exponent of growth (growth rate order)
$K_d$	molar coefficient for diffusional mass transport, $\text{mole m}^{-2} \text{s}^{-1}$
$K_r$	molar coefficient for surface reaction step, $\text{mole m}^{-2} \text{s}^{-1}$
$k_d$	coefficient for diffusional mass transport, $\text{kg}_0 \text{ m}^{-2} \text{s}^{-1}$

$k'_d$	coefficient for diffusional mass transport, $\text{kg}_0 \text{ kg}^{-1} \text{ m s}^{-1}$
$k'_G$	kinetic constant of crystal growth, $\text{kg}^{1-g} \text{ kg}_0^g \text{ m}^{-2} \text{ s}^{-1}$
$k'_G$	kinetic constant of crystal growth, $\text{kg}^{-g} \text{ kg}_0^g \text{ m s}^{-1}$
$k_r$	kinetic constant for surface reaction step, $\text{kg}^{1-r} \text{ kg}_0^r \text{ m}^{-2} \text{ s}^{-1}$
$k'_r$	kinetic constant for surface reaction step, $\text{kg}^{-r} \text{ kg}_0^r \text{ m s}^{-1}$
$L$	characteristic crystal size, m
$\dot{L}$	linear crystal growth rate, $\text{m s}^{-1}$
$\dot{l}$	linear growth rate of crystal face, $\text{m s}^{-1}$
$M_{\text{hyd}}$	molar mass of hydrate, $\text{kg mole}^{-1}$
$M_m$	average molar mass, $\text{kg mole}^{-1}$
$M_{\text{H}_2\text{O}}$	molar mass of water, $\text{kg mole}^{-1}$
$m_c$	mass of crystal, kg
$\Delta m_c$	mass increase, kg
$m_{c0}, m_{cc}$	initial and final mass of crystals, kg
$\dot{m}_A$	mean mass crystal growth rate related to the crystal surface area, $\text{kg m}^{-2} \text{ s}^{-1}$
$N_c$	number of crystals
$q$	auxiliary variable in Eq. (18)
$R$	universal gas constant, $\text{J mole}^{-1} \text{ K}^{-1}$
$r$	kinetic exponent of surface reaction
$T$	temperature, °C. K
$t$	time, s
$t_c$	duration of growth, s
$V$	volume, $\text{m}^3$
$v$	flow rate of solution, $\text{m s}^{-1}$
$w$	concentration, $\text{kg kg}_0^{-1}$
$w_i$	concentration at the crystal-liquid interface, $\text{kg kg}_0^{-1}$
$w_{\text{eq}}$	solubility, $\text{kg kg}_0^{-1}$
$\Delta w$	supersaturation, $\text{kg kg}_0^{-1}$
$y$	mole fraction of hydrate
$y_i$	mole fraction of solute at the interface
$y_{\text{eq}}$	solubility
$\alpha$	volume shape factor
$\beta$	surface shape factor
$\nu$	kinematic viscosity, $\text{m}^2 \text{ s}^{-1}$
$\rho_c$	crystal density, $\text{kg m}^{-3}$
$\rho_l$	solution density, $\text{kg m}^{-3}$
$\psi$	sphericity

## REFERENCES

1. Nývlt J., Söhnel O., Matuchová M., Broul M. in: *The Kinetics of Industrial Crystallization*, p. 193, Academia, Prague and Elsevier, Amsterdam 1985.
2. McCabe W. L., Stevens R. P.: *Chem. Eng. Prog.* **47**, 168 (1951).
3. Ref.<sup>1</sup>, p. 152.
4. Hixson A. W., Knox K. L.: *Ind. Eng. Chem.* **43**, 2144 (1951).
5. Tai C. Y., Pan R. K.: *J. Chin. Inst. Chem. Eng.* **16**, 379 (1985).
6. König A.: *Thesis*. Bergakademie, Freiberg 1984.
7. Karel M., Nývlt J.: *Collect. Czech. Chem. Commun.* **54**, 2951 (1989).



8. Karpiński P.: *Mass Crystallization in a Fluidized Bed*. (Scientific papers of the Institute of Chemical Engineering No. 40, Technical University Wroclaw). Wydawnictwo Politechniki Wroclawskiej, Wroclaw 1981.
9. Matuchová M.: *Thesis*. Prague Institute of Chemical Technology, Prague 1974.
10. Matuchová M., Nývlt J.: *Chem. Prum.* 25, 463 (1975).
11. Kočová H., Nývlt J.: *Chem. Prum.* 22, 165 (1972).
12. Karel M., Nývlt J.: *Chem. Eng. Commun.* 61, 319 (1988).
13. Toyokura K., Uchiyama M., Kawai M., Akutsu H., Ueno T.: in the book: *Industrial Crystallization 81* (S. J. Jančič and E. J. de Jong, Eds), p. 87. North-Holland, Amsterdam 1982.
14. Chhun T., Couderc J. P.: *Chem. Eng. Sci.* 35, 1707 (1980).

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