

## RATE OF GROWTH OF CITRIC ACID CRYSTALS

J. NÝVLT and V. VÁCLAVŮ

*Research Institute of Inorganic Chemistry, Ústí nad Labem*

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A relation is derived describing generally the dependence of the rate of crystal growth on supersaturation and a comparison is made with the empirical relation mostly used for this dependence. The explanation is given why in a number of cases the exponent of the concentration dependence of the crystallization rate is not an integer. Theoretical considerations are illustrated by the crystallization rates of citric acid.

The crystal growth can be described by the following simplified model: there exists a stationary layer of solution on the crystal surface which is in dynamic equilibrium with the crystal surface on the one hand and with the bulk phase of the supersaturated solution on the other hand. The proper crystallization process takes place in several stages: 1) Mass transfer to the surface of this layer, 2) diffusion of matter through the stationary layer of solution on the crystal surface, 3) particle motion on the crystal surface and their positioning into the crystal lattice, 4) transfer of heat of crystallization and, if any, of the liberated hydration water from the crystal surface.

The kinetics of crystal growth is in general<sup>1</sup> said to be determined by the slowest of these operations *i.e.* by diffusion or by the positioning of particles into the crystal lattice.

The first of these operations is expressed by the Fick's law  $\dot{m} = k_d A (c - c_k)$  where  $k_d = D/\delta$ ;  $\dot{m}$  is the rate of crystal growth,  $D$  diffusion coefficient,  $\delta$  width of diffusion layer,  $c$  and  $c_k$  concentrations in solution and at the crystal surface of area  $A$ . The theoretical relations describing the kinetics of positioning of particles into the crystal lattice<sup>2,3</sup> are very complex, nonetheless, they can be approximated by relation  $\dot{m} = k_1 A (c_k - c_s)^i$  where exponent  $i$  becomes according to the conditions  $i = 1$  or  $i = 2$  and  $c_s$  is solubility. If the unknown concentration closely at the crystal surface,  $c_k$ , is eliminated from these equations, relation<sup>4,15</sup> is obtained

$$\dot{m}/k_1 A = [\Delta c - (\dot{m}/k_d A)]^i, \quad (1)$$

where  $\Delta c = c - c_s$ . If the value of  $k_d$  is relatively large the second term on the right hand side of Eq. (1) may be neglected and relation  $\dot{m} = k_1 A \Delta c^i$  is obtained according to which the kinetics of crystal growth is controlled by the kinetics of positioning of particles into the crystal lattice. On the contrary, for large  $k_1$  the right hand side of Eq. (1) must approach zero, thus  $\dot{m} = k_d A \Delta c$  and the crystallization kinetics is controlled by diffusion. For cases situated in between these extremes there is currently used the empirical relation

$$\dot{m} = k_g A \Delta c^g, \quad (2)$$

in which the kinetic constant of the growth  $k_g$  and the order of equation  $g$  have the nature of adjustable parameters, and can be considered constant for certain usually not too wide concentration ranges. Value of the exponent  $g$  is very often close to 1.0 (e.g.  $5^{-8}$ ) or 2.0 (e.g.  $9^{-12}$ ) but also values in between 1.0 and 2.0 are published<sup>13-15</sup>, but without any quantitative explanation.

### THEORETICAL

On basis of the general Eq. (1), two possible values of the exponent  $i$  follow from theories of positioning of particles into the crystal lattice:

a) For  $i = 1$  Eq. (1) is simplified to the familiar<sup>16-18</sup> form

$$\dot{m} = \left( \frac{1}{k_i} + \frac{1}{k_d} \right)^{-1} A \Delta c \quad (3)$$

while b) for  $i = 2$  Eq. (1) takes the form

$$(k_i/k_d^2 A) \dot{m}^2 - (1 + 2 \Delta c k_i/k_d) \dot{m} + k_i A (\Delta c)^2 = 0 \quad (4)$$

with the trivial solution

$$\dot{m} = (A/2k_i k_d^{-2}) [1 + 2 \Delta c k_i/k_d - (1 + 4 \Delta c k_i/k_d)^{1/2}], \quad (5)$$

where the negative sign of the square root results from the boundary condition  $\dot{m} = 0$  for  $\Delta c = 0$ .

Now let us assume, that this dependence of  $\dot{m}$  on  $\Delta c$  should be satisfactorily represented in a limited range of supersaturations by the empirical function (2). From

TABLE I

Values of the Empirical Exponent  $g$  as Function of Variable  $z = (k_i/k_d) \Delta c$   
Value  $y$  is calculated from the right hand side of Eq. (6).

$z$	$y$	$g$	$z$	$y$	$g$
0.001	1.0000	2.000	1.5	0.3009	1.411
0.005	0.9902	1.994	2.0	0.2500	1.355
0.01	0.9805	1.986	3.0	0.1886	1.304
0.05	0.9110	1.954	4.0	0.1524	1.261
0.1	0.8392	1.864	5.0	0.1283	1.228
0.3	0.6487	1.716	10	0.0730	1.186
0.5	0.5359	1.626	50	0.0174	1.109
0.7	0.4598	1.545	100	0.0090	1.049
0.9	0.4044	1.489	$10^3$	0.0010	1.046
1.0	0.3820	1.461	$10^4$	0.0001	1.000

the equivalence of relations (2) and (5) it follows:

$$(k_g/k_i) \overline{\Delta c}^{g-2} = y = 1/2 [1 + 2z - (1 + 4z)^{1/2}] z^{-2}, \quad (6)$$

where  $z = x \overline{\Delta c}$ , and  $x = k_i/k_d$ , where  $\overline{\Delta c}$  is the logarithmic mean in the interval  $\Delta c_{\min}$  to  $\Delta c_{\max}$  covered by experiments. From Eq. (6) there follows the relation

$$d \log y / d \log \overline{\Delta c} = d \log y / d \log z = g - 2 [x = \text{const.}], \quad (7)$$

which makes possible the calculation of the empirical exponent  $g$  from the corresponding values of variable  $z$ . The dependence of  $y$  or  $g$  on  $z$  is given in Table I from which it is obvious that the exponent  $g$  may be of any value between 1.0 and 2.0.

### EXPERIMENTAL

The citric acid crystallizes at temperatures above 36.6°C as anhydrous, at temperatures below 36.6 as a monohydrate<sup>19</sup>. Since the literature data<sup>20</sup> concerning this acid are very limited its crystallization rate in aqueous solutions was determined for cases given in Fig. 1. The measurement was made by the formerly described method<sup>7</sup> of weighing a monocrystal suspended in a supersaturated, agitated solution. Obtained values are plotted in Fig. 1 in logarithmic coordinates and for the drawn straight lines the values of their slopes  $g$  were determined and from those the values of constants  $k_g$  were calculated.

### RESULTS AND DISCUSSION

For individual groups of measurements mean supersaturation values  $\overline{\Delta c}$  were calculated. By interpolating in Table I the values of  $z$  corresponding to the individual values  $g$  were determined and the corresponding values  $x$  and  $y$  were calculated. Values

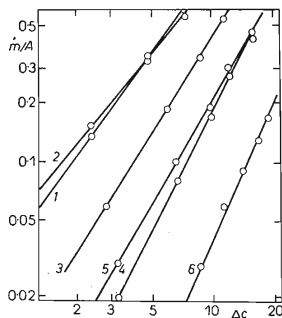


FIG. 1  
Growth Rate of Citric Acid Crystals  $\dot{m}/A$  ( $\text{kg m}^{-2} \text{h}^{-1}$ ) in Dependence on the Supersaturation  $\Delta c$  ( $\text{g}/100 \text{ g H}_2\text{O}$ )  
Anhydrous acid: 1 70°C; 2 70°C with 1% of  $\text{H}_2\text{SO}_4$ ; 3 43°C. Monohydrate: 4 32°C; 5 32°C with 1% of  $\text{H}_2\text{SO}_4$ ; 6 12°C.

$k_i$  were calculated from thus obtained  $y$  and  $k_d$  using  $x$ . The results of calculation are summarized in Table II (values  $\Delta c$  and  $\dot{m}/A$ , Fig. 1). From the results of calculation it follows, that while diffusion at crystallization of anhydrous citric acid and monohydrate takes place at about the same rate (with the exception of the last series of measurements at the lowest temperature where the integration into the crystal lattice is very slow and no quantitative data on the diffusion rate can be obtained), the integration step for the anhydrous citric acid is faster by several orders than with the monohydrate. An addition of sulphuric acid accelerates positioning into the crystal lattice but it somewhat hinders diffusion. The activation energy of positioning of particles into the crystal lattice calculated from the analogy of Arrhenius relation gives in both cases values about 15 kcal/mol, while the activation energy of diffusion cannot be calculated from these data but obviously will be substantially smaller. As it was possible to expect, the rate of the particle incorporation into the crystal lattice increases with increasing temperature which is represented by a lower value of the empirical exponent  $g$ : more and more diffusion becomes the controlling operation.

## CONCLUSIONS

The assumption according to which the order of positioning of particles into the crystal lattice equals  $i = 1$ , and on which the usual use of the kinetic equation for the rate of crystal growth of the type (3) is based, is generally very improbable. But this assumption appears not to be necessary and the given equation is the limiting case of the more general Eq. (5) for  $i = 2$ . The second limiting case of the given Eq. (5) is relation  $\dot{m} = k_i A \Delta c^2$  and in case one of these two equations is not valid, the rate

TABLE II

### Crystallization Rate of Citric Acid

The symbol  $\Delta c$  in units of kinetic constants stresses that the constant is related to supersaturation (expressed as kg per kg of free solvent) with the corresponding exponent.

Curve	$k_g$ $\text{kg m}^{-2} \text{h}^{-1} \Delta c^{-g}$	$g$	$z$	$x$	$y$	$k_i$ $\text{kg m}^{-2} \text{h}^{-1} \Delta c^{-2}$	$k_d$ $\text{kg m}^{-2} \text{h}^{-1} \Delta c^{-1}$
1	22.8	1.36	2.2	52	0.234	735	14.0
2	14.3	1.21	5.8	138	0.114	1 590	11.5
3	21.4	1.65	0.45	7.5	0.560	102	13.5
4	14.2	1.90	0.09	1.1	0.852	21.5	19.6
5	10.3	1.70	0.37	4.6	0.603	36.4	7.9
6	4.5	2.0	0.00	0.0	1.000	4.5	—

of crystal growth would have to be expressed by the complicated function (5). If this function is, for narrow range of supersaturations, approximated by empirical Eq. (2) we must expect the value of the exponent  $g$  to vary continuously with temperature, relative velocities of the solution and the crystal, eventually other parameters. The exponent  $g$  may have in this case any value between 1.0 and 2.0. The experimental data for the rate of crystal growth of citric acid from aqueous solutions and their evaluation by the derived relations give dependences which could have been qualitatively expected.

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