RATE OF GROWTH OF SODIUM THIOSULPHATE CRYSTALS

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The crystallization rate of sodium thiosulphate from aqueous solutions was measured at 30°C and at various relative velocities of crystals and solution. The rate of crystal growth may be expressed by a kinetic equation of the first order, dependence of the rate constant on the flow rate was expressed by use of dimensionless numbers.

In the frame of studies on crystallization of inorganic materials, the crystallization of sodium thiosulphate was dealt with. It is a substance which crystallizes relatively well in large, well developed crystals and for this reason it was chosen for a detailed study of the effect of flow velocity on the rate of crystal growth.

The rate of crystal growth may be, in a limited range of supersaturations[1], expressed by an empirical equation $dm/dt = k_g A \Delta c^g$ according to which the increase of the mass of crystals dm in a time interval dt is proportional to its surface area A and certain power of supersaturation Δc. The constant of rate of crystal growth k_g and the order of the kinetic equation of growth g may be taken as constants dependent among others on diffusion as the first particular operation and positioning of particles into the crystal lattice as the second particular operation of the crystal growth. It is obvious that the relative velocity between the solution and the crystal will greatly affect the rate of the diffusion step and thus it will affect the value of the constant k_g and in some cases[1] the value of the exponent g as well. In the limiting case, when diffusion may be taken as the controlling operation holds that $k_g = D/\delta$ where D is the diffusion coefficient and δ the width of the diffusion layer. If we assume that the kinetics of incorporation of particles into the crystal lattice may be expressed similarly as the diffusion by the first order equation, then holds

$$k_g = (\delta/D + 1/k_i)^{-1}, \qquad (1)$$

where k_i is the rate constant of the reaction step. Thus if the value of δ is expressed as a function of relative velocity between the crystal and solution, the dependence of k_g on this parameter is known[2] as well. The assumption that the reaction step may be described by the kinetic first order equation is, in reality, in spite of its frequent use in crystallization literature, very dubious and thus the dependence of the rate constant of crystal growth on the flow rate of solution is very frequently expressed by use of dimensionless numbers.

Mullin[3] *e.g.* presents the equation in the form

$$\text{Sh} = \text{const.} \, \text{Re}^a \cdot \text{Sc}^{1/3}, \qquad (2)$$

where the Sherwood number is given by relation $\text{Sh} = k_g L/D$, the Schmidt number by $\text{Sc} = \eta/\varrho_1 D$ and the Reynolds number by $\text{Re} = uL\varrho_1/\eta$. Here, ϱ_1 and η are density and viscosity of the solu-

tion, L the characteristic size of the crystal and u the relative velocity between the crystal and solution. The empirical exponent a given in literature equals most often to size $a = 0.6$.

EXPERIMENTAL AND RESULTS

The crystallization rate of sodium thiosulphate was measured in an apparatus with a fluidized bed of crystals described in the previous paper[4]. The changes of flow velocity around crystals may be in experimenting with a fluidized bed realized by use of crystals of different sizes. In this case a simple idea is applied that the upward velocity of solution which keeps the crystals fluidized equals to the settling velocity of particles. If a small number of crystals is used (20—50) the fluidized bed is very thin and this assumption can be accepted as reasonable.

The settling velocities were measured in a slightly superheated solution (at 25°C, superheating for to 0·5°C) so as to prevent nucleation, in a pipe of ID 30 mm between two prints 770 mm apart. For measurement there were used eight narrow fractions obtained by a sieve separation. The flow rate of solution through the apparatus was varied by use of a set of calibrated nozzles in the range of 300 to 800 ml/min so that the crystals present in the measuring tube were uniformly fluidized.

Eight crystal fractions in the range of size 0·6 to 4·0 mm were used also for measurement of the crystallization rate. The calculation of the rate constant of crystal growth was made with use of relation[4]

$$k_g^{(g)} = (3\alpha^{2/3}\varrho_c^{2/3}/\beta) \cdot (m^{1/3} - m_o^{1/3})/(N^{1/3}t\,\Delta c^g)\,, \tag{3}$$

where $\alpha = 0.45$ is the volumetric shape coefficient, $\beta = 3.8$ is the surface shape coefficient, $\varrho_c = 1\,685$ kg/m^3 is the density of crystals, m_0 and m the weight of crystals at the beginning and at the end of the experiment (kg), N is the number of crystals used for the measurement, t is the time (h) and Δc is supersaturation (kg/m^3). The supersaturation Δc was calculated from the experimentally fixed value of ΔT according to relation $\Delta c = 7.2\,\Delta T$. The value of the order of the kinetic equation of crystal growth g was determined from the dependence of linear rate of crystal growth

$$\dot{L} = [(m/\alpha\varrho_c N)^{1/3} - (m_0/\alpha\varrho_c N)^{1/3}]/t \tag{4}$$

TABLE I

Settling Velocities and the Growth Rates of Na$_2$S$_2$O$_3$. 5 H$_2$O Crystals of Various Sizes

Fraction mm	u cm/s	$k_g \cdot 10^1$ m^3 m^{-2} h^{-1}	Standard deviation, %	
			individ. measur.	average
0·6 —0·8	1·26	1·28	8·4	2·4
0·8 —1·0	1·53	1·26	7·5	2·4
1·0 —1·25	1·97	1·49	7·4	2·0
1·25—1·5	2·73	1·95	4·1	1·1
1·5 —2·0	2·98	2·01	5·3	1·4
2·0 —2·5	3·30	2·12	4·6	1·3
2·5 —3·0	4·14	2·01	4·4	1·2
3·0 —4·0	4·94	2·06	4·4	1·3

on supersaturation, as the slope of straight line representing this dependence in logarithmic coordinates.

The results obtained by evaluating the experimental data by the least square method are given in Table I. The evaluation was made by use of dimensionless numbers or by Eq. (2) arranged in the form

$$\log(k_g L) = \log C + a \log(uL), \qquad (5)$$

where $C = \text{const. } D^{2/3}(\varrho_1/\eta)^{a-1/3}$ and L is the size of crystals. This equation enables linearization of the dependence k_g on u. The slope of the most probable straight line drawn through the experimental points of the dependence $\log k_g L$ on $\log uL$ corresponds to the exponent a and has a value $a = 0.75$. Though this value is somewhat larger than the value 0.6 usually cited in literature, it is reasonable; $C = 1.25 \cdot 10^{-3}$.

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