

The Crystal Growth of Sparingly Soluble Salts*

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The mechanism of crystal growth of sparingly soluble salts from their supersaturated solutions is discussed in the light of a number of available growth theories. It is shown that in the case of both calcium sulphate and calcium carbonate, the observed quadratic dependence of the rate of crystallization upon the relative supersaturation is consistent with a surface controlled reaction. The reaction rates are unaffected by changes in the fluid dynamics within the crystallization cell, and the activation energy for both seeded growth and the linear growth of calcium sulphate is 15.0 ± 0.5 kcal mole⁻¹. Evidence is discussed for a screw dislocation mechanism for calcium sulphate crystal growth. Under conditions of relatively high supersaturation, secondary nucleation of both calcium sulphate and calcium carbonate crystals is observed upon the addition of seed crystals. The striking effect of certain additives in reducing the rate of crystal growth is discussed in terms of the important factors involved and in a number of instances it is shown that a simple adsorption isotherm of the Langmuir type satisfactory describes the growth data.

The precipitation and crystal growth of sparingly soluble salts from solution has been widely studied and a number of apparently conflicting results and theories have appeared¹⁻⁶. For the present discussion, we may represent a typical crystal surface as in Fig. 1. The first detailed theoretical treatment of

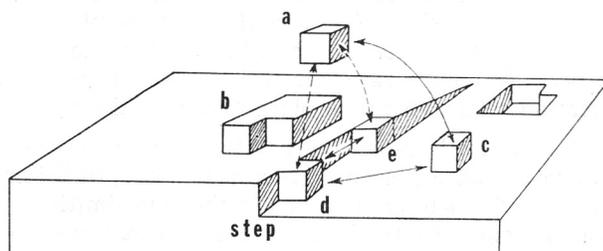


Fig. 1. Representation of a crystal surface showing the development of an edge or step, a surface nucleating site and an etch pit.

crystal growth was given by Kossel⁷ and Stranski⁸ and developed by Becker and Doring^{9,10}. In terms of this model of stepwise growth, there are non-equivalent sites on a crystal surface. An ion may be adsorbed onto a smooth surface, an edge or step, or a kink site (position e, Fig. 1). Of these, the kink site is prefer-

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red while the edges and corners are less favorable. The adsorption theory of crystal growth is built upon this model which involves the formation of surface nuclei [position (b), Fig. 1], the spreading of these into rows of ions and the joining together of the rows to form monolayers, which, when placed on top of one another build up the crystal lattice. The first step in the formation of a new layer has particularly unfavorable energy requirements. If the formation of such a surface nucleus is rapid, a new layer may start before the growth of the preceding layer is complete leading to polynuclear growth. If the formation of surface nuclei is very slow however, one layer is formed after the last is complete (mononuclear growth) and this type of growth is therefore strongly inhibited energetically. At low supersaturations the formation of a surface nucleus is unlikely and in terms of this model, crystal growth should be detected only after an appreciable supersaturation has been attained. In practical cases, however, experiments have shown that many crystals actually grow at supersaturations below 1%¹¹ whereas the surface nucleation theory would require levels of supersaturation of 25–50% in order to ensure two dimensional nucleation on each completed lattice layer on the crystal surface. Frank^{12,13} showed that even when assisted by surface diffusion it would not appear possible to explain the rate of spreading of layers by such a repeatable step mechanism. Frank pointed out that real crystals are imperfect and contain dislocations. Such a screw dislocation as shown in Fig. 1, emergent at a crystal surface would offer a perpetual step for crystal growth and avoid the necessity for two-dimensional nucleation.

In terms of the surface dislocation model, the process of deposition of new material upon a crystal face (Fig. 1) may be expected to take place through a number of simple stepwise events. (i) the transport, within the bulk solution phase, of ions, atoms or molecules from position (a) up to the crystal surface. (ii) At the surface, the unit may become attached to the face (position c) by a process of adsorption or chemisorption and thereafter, (iii) undergo two dimensional diffusion to a neighbouring site (position d) offering an energetically more favorable position at an edge or step on the crystal surface. (iv) A one dimensional diffusion along the step to a kink, places the seed unit in an even more favorable energetic position (e) with three of its planes in contact with the crystal surface. (v) Attachment at the kink with concomitant dehydration, completes the process of incorporation into the crystal lattice. The dehydration or partial dehydration might also take place in any of the steps (ii) through (v).

The observed reaction kinetics for crystal growth reflects the slow step or steps in the above model for crystal growth. If the equilibrium at the crystal face is sufficiently rapid not to be involved in the rate-limiting step, the crystal growth is controlled by step (i), the bulk diffusion of material up to the surface. Under these circumstances the rate of crystal growth ($-dm/dt$) would be expected, through Fick's law of diffusion, to be proportional to the supersaturation ($m - m_0$) where m = molar concentration of solute at time t and m_0 is the value of m at equilibrium (solubility). There is now considerable evidence for numerous electrolytes that the rate of crystallization is not simply a bulk diffusion reaction^{14,15} with a rate varying linearly with supersaturation. The screw dislocation model developed by Burton, Cabrera, and Frank^{12,13} for a system of non-dissociated species growing from the vapor phase, was applied by Chernov¹⁴ to crystallization systems involving liquid-solid phase transitions.

In a discussion of surface controlled reactions, Reich and Kahlweit¹⁵ extended this theory and derived the equation

$$-(m - m_0) = \frac{dm/dt}{k_D} + \left(\frac{dm/dt}{k_R} \right)^{1/2} \quad (1)$$

where k_D and k_R are the rate constants for a diffusion-controlled and surface-controlled reaction, respectively. Under conditions of low supersaturation where the rate of crystal growth is small, $k_D > k_R$ and

$$\frac{-dm}{dt} \approx k_R (m - m_0)^2 \quad (2)$$

For large growth fluxes, however, the diffusion process becomes more important and

$$\frac{-dm}{dt} \approx k_D (m - m_0) \quad (3)$$

Thus at low supersaturations the growth rate dependence on supersaturation is parabolic while at high supersaturations the dependence is linear. In the former case, the turns of the growth spiral become close enough in order to compete directly for ions from the bulk of the solution. An expression similar to that shown in equation (2) was derived by Davies and Jones¹⁶ in terms of a model for crystal growth incorporating an adsorbed monolayer at the crystal surface. This theory was also successful in explaining the observed parabolic dependence upon supersaturation under conditions in which non-equivalent ionic concentrations of lattice ions were present in the supersaturated solutions⁴.

Recently¹⁷⁻²¹ studies have been made of the mechanism of crystallization of the sparingly soluble salts calcium sulfate and calcium carbonate. Both these salts are involved in desalination processes through the formation of scale on heat transfer surfaces²². In addition, calcium carbonate crystallization may play a major role in the carbonate buffering of sea water²³. Many investigations have been concerned with the measurement of concentration changes accompanying spontaneous precipitation from supersaturated solutions on the assumption that homogeneous nucleation takes place. It is impossible, however, to ensure the absence of heterogeneous nucleation in such systems and in an attempt to eliminate this uncertainty, the present work has been concerned with the growth of seed crystals in supersaturated solutions of calcium sulfate and calcium carbonate. By the careful control of experimental conditions, it is possible to prepare stable supersaturated solutions and, following inoculation with well-characterized seed crystals, the rate of crystal growth can be determined by measuring the concentrations of lattice ions as a function of time and by microscopic examination of the growing crystals.

The growth of calcium sulfate dihydrate crystals has been found to follow the kinetic equation (4)

$$\frac{-dm}{dt} = k_c s_n (m - m_0)^2 \quad (4)$$

which is similar to equation (2). In equation (4), $m (= [\text{Ca}^{2+}] = [\text{SO}_4^{2-}])$ represents the concentrations of free ions, s_n is a function of the number of

growing sites added as seed crystals and k_0 is the rate constant for growth. A typical plot of the integrated form of equation (4) is shown in Fig. 2 for which the initial calcium sulfate concentration of the stable supersaturated solutions, 3.94×10^{-2} M, may be compared with the solubility value 2.04×10^{-2} M. In this experiment, the concentration of seed crystals was 252 mg/100 ml²⁴. The rate constant for crystal growth of calcium sulfate dihydrate

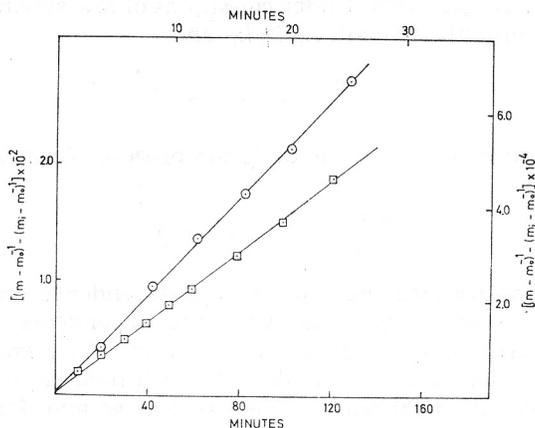


Fig. 2. Quadratic dependence upon degree of supersaturation of the rate of growth of calcium sulfate (curve 1) and calcium carbonate (curve 2) plotted according to the integrated forms of equation (4). Lower abscissa and left-hand ordinate scales refer to calcium sulfate. Upper abscissa and right-hand ordinate scales refer to calcium carbonate.

is independent of the stirring rate between 100 and 300 r. p. m. again pointing against diffusion as the rate controlling mechanism. The activation energy for the reaction, 15.0 ± 0.5 kcal mole⁻¹ is considerably larger than that to be expected for a bulk diffusion reaction adding further evidence for the proposed interface process. During the crystallization reaction, the mass of calcium sulfate dihydrate deposited is as much as three times the weight of the original seed crystals. It is interesting to note, however, that equation (4) satisfactorily describes the growth data despite the appreciable increase in surface area during the course of the experiments. A similar observation was made in the crystal growth of magnesium oxalate²⁵ and the result is consistent with the idea that no new growth sites are formed during crystallization. It is likely that growth is confined to screw dislocations present on the seed crystals added to initiate the reaction and that few, if any, new growth sites are created during the course of the experiment.

Under conditions of higher supersaturation, secondary nucleation takes place initially when the seed crystals of calcium sulfate are added to the supersaturated solution. Microscopic evidence suggests that this secondary nucleation probably takes place both on the surface of the crystals and in the bulk of the solution. The existence of secondary nucleation has been recognized for some time by those interested in industrial crystallization but it is only relatively recently that it has been invoked in kinetic studies of crystal growth²⁵⁻²⁸. Under conditions in which the rate of growth is rapid, the seed crystals may grow as a polycrystalline mass which breaks up to provide additional crystals for growth. Alternatively²⁹, the secondary nucleation may

be due to collision breeding in which large numbers of crystals may be formed when the seed particles collide with each other or slide over the surfaces of the crystallization cell. The latter explanation appears to be more likely in the stirred systems of interest in this paper.

The experiments described above yield results relating to the crystal growth of calcium sulfate dihydrate crystals averaged over all faces of the seeding crystals. In such studies of the kinetics of crystal growth, in addition to following concentration changes in the supersaturated solution, observation of the growing crystals themselves is clearly of considerable importance. A study of the linear crystallization rate of calcium sulfate dihydrate from supersaturated solution has recently been completed¹⁸, and the activation energy of the fast growing faces has been determined by observing the rate of growth as function of temperature. The growth rate, expressed in mm/min follows an equation

$$R = k_1 (T_{Ca} - T_{Ca}^0)^2 \quad (5)$$

which is very similar to the parabolic dependence upon supersaturation in equation (4). In equation (5), k_1 is the rate constant for linear growth, T_{Ca} represents the total calcium concentration of the supersaturated solution, and T_{Ca}^0 is the solubility value at the particular ionic strength. The results of the direct measurements of the growing crystals are therefore consistent with the averaged growth rate experiments. Moreover, the calculated activation energies, 16 ± 1.5 kcal mole⁻¹ for linear growth and 15.0 ± 0.5 kcal mole⁻¹ for averaged growth are in excellent agreement.

Its crystal growth behavior, calcium carbonate behaves similarly to calcium sulfate dihydrate¹⁹⁻²⁰ and a plot of the integrated form of equation (4), with $m = [Ca^{2+}]$, is included in Fig. 2 for comparison. The observed lack of stirring rate dependence of the rate constant and the experimentally determined activation energy of 11.0 kcal mole⁻¹ support the proposed surface-controlled mechanism for crystal growth. Under conditions of higher supersaturation and lower seed concentrations, growth is preceded by an initial growth surge in which the rate is faster than that to be expected from the kinetic equation (4). Microscopic examination of the crystals again confirms an additional secondary nucleation reaction with concomitant surface roughening of the seed crystals. At lower supersaturations and higher seed concentrations, the crystal growth process predominates over that of nucleation and the crystals maintain the smooth appearance of the original seed crystals.

The striking effect of additives in reducing the rate of crystallization has been described for a number of systems. In many instances the results of such experiments are useful in helping to elucidate the mechanism of the crystallization process. The following factors have to be considered in analyzing the results of such experiments.

a) The added ions may form stable complexes with one of the lattice ions of the precipitating solid. The effective concentration of the lattice may therefore be reduced in the presence of the foreign ion and the rate of crystallization will be lowered.

b) The additive may be adsorbed at growth sites on the crystal surface and effectively prevent further deposition of solid. The effect may result in a complete inhibition of crystal growth.

c) In the event that adsorption takes place only at certain crystal sites, however, the remaining faces may continue to grow at normal or near normal rates. In the latter case, the additive will have a marked effect upon the morphology of the growing crystals.

d) The additive, if ionic, will change the ionic strength of the supersaturated solution and hence the effective solubility of the precipitating phase. Since the concentration of added foreign ions is usually small, however, this factor is likely to be of considerably less importance than those outlined above.

The excellent reproducibility of the calcium sulfate dehydrate and calcium carbonate crystal growth experiments enables quantitative studies to be made of the effect of additives upon the rate of crystallization^{21,30}. The phosphonic acid derivatives form a particularly interesting series of additives since they inhibit crystal growth when present at concentrations as low as 5×10^{-8} M. At such concentrations possible effects due to calcium ion complexation [point (a) above] can be ruled out. Indeed, in the adsorption of additive, considerably less than 1% of the effective crystal seed surface will be covered by the added phosphonate despite complete inhibition of the growth reaction. This indicates that a relatively small number of growth sites are active in the crystallization process and this suggestion is consistent with a screw dislocation mechanism. Strong adsorption of phosphonate ions may take place through the formation of complexes with the calcium ions at the crystal surface. If it is assumed that the additive molecules are adsorbed on growth sites on the surface of the growing crystals, their presence will prevent deposition of material near these growth sites. If a fraction Θ of the available sites is occupied by the added ion when its concentration is $[A]$ then the inhibiting influence may be expressed in terms of a simple Langmuir-type adsorption isotherm. If the rate of adsorption is written $k_1 [A](1 - \Theta)$ and the rate desorption is k_2 , where k_1 and k_2 are the corresponding rate constants, at equilibrium these rates are equal and $\Theta = k_1 [A]/k_1 [A] + k_2$. Writing $(k'_c s'_n)$ as the value of $(k_c s_n)$ in the absence of contaminant, we have

$$\frac{1}{k'_c s'_n - k_c s_n} = \frac{1}{k'_c s'_n (1 - b)} + \frac{k_2}{k_1 [A] k'_c s'_n} \quad (2)$$

where b is a constant; $b(k'_c s'_n)$ being the limiting value of the rate constant with additive present.

It is interesting to note that a simple Langmuir type isotherm satisfactorily describes the marked inhibiting effect in terms of a monomolecular layer of foreign ions at growth site on calcium carbonate crystals²¹.

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IZVOD

Rast kristala slabo topljivih soli

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Prikazano je sadašnje stanje teorije rasta slabotopljivih soli iz vodenih otopina. Na primjerima rasta kristala kalcium-sulfata dihidrata i kalcium-karbonata prikazani su i dosadašnji rezultati iz autorovog laboratorija. Izmjerene energije aktivacije za rast kristala, 15 kcal/molu za sulfat i 11 kcal/molu za karbonat, znatno su veće od onih koje su mjerene za difuziju u otopinama. To ukazuje, da se kontrola reakcije nalazi u stupnju koji se odvija na samoj površini kristala. Eksperimenti s inhibitorima (fosfonska kiselina) pokazuju da su već dovoljne i vrlo male koncentracije tih tvari (5×10^{-8} M) da obustave rast kristala, iako je manje od 1% površine prekriveno adsorbiranim inhibitorom.

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