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Conference Paper

Precipitation and Crystal Growth from Solution

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The precipitation of crystals from solution involves nucleation, which is usually rapid and heterogeneous, and the subsequent growth of the crystals. In order to measure the rate of the interface growth process, the size of the crystals, as well as the rate of incorporation of material into the crystals, must be measured, and very small crystals must be studied to insure interface control.

For slightly soluble salts the order of the interface growth process depends upon the stoichiometry of the salt and its supersaturation. The interface growth coefficients for different salts, orders of crystallization, and supersaturation are compared. These coefficients depend upon the type of salt crystallizing, but usually not upon the order or supersaturation.

INTRODUCTION

Precipitation of crystals from solution is important in analytical chemistry and in many industrial processes. Crystals grown from solution are often strikingly beautiful, as well as being of scientific and technical importance. Nucleation and growth processes can be studied during precipitation, leading to new insight into important phenomena in phase transformations.

The literature of studies in this area is vast. Van Hook's book emphasizes crystallization from solution and industrial practice¹. Nielsen reviews kinetics of precipitation and lists an extensive bibliography². Mechanisms for crystal growth from solution are discussed in a number of research papers, including references³⁻⁸.

In this paper the various experimental techniques used to study the rate of precipitation and crystal growth from solution are described; then some remarks about nucleation are made, and various growth laws summarized. Then values of interface growth coefficients and the order of growth kinetics, as measured by various authors on different slightly soluble salts, are summarized. Evidence for coagulation of crystals during precipitation is shown, and some comments on growth theories are made.

EXPERIMENTAL METHODS

Crystal growth from solution can be induced in several different ways. Two solutions of soluble salts can be mixed to give a supersaturated solution for an insoluble salt with an ion from either solution. This method is somewhat irreproducible, since the number of nuclei formed depends upon the method of mixing. However, if the crystal growth is slow compared to the time of mixing this method is often satisfactory, and is also the closest to usual industrial practice. A supersaturated solution can also be developed by generating one ion of a salt slowly and homogeneously with a chemical reaction, but this method requires additional ionic or other impurities in the solution. Addition of seed crystals to a slightly

supersaturated solution and observation of subsequent growth has the advantage that the size of the seed crystals can be measured before their addition to the solution.

The rate of precipitation is usually measured from the conductance of the solution or from analysis of the solution separated from crystals. These methods measure only the total amount of precipitated material, and give no measurement of crystal size. If the crystals are large enough their size or number can be measured in the optical microscope or with special counters during or after precipitation. Such measurements often miss small crystals, and can give misleading results if the crystals coagulate. I have measured the light scattered from precipitating barium and strontium sulfate crystals at the same time as the conductance, from which both the particle size and therefore the specific growth coefficient can be calculated^{9,20}. The particle size can be measured in the electron microscope, but the solution must be evaporated away in this technique, so that the final morphology of the crystals can be influenced by the evaporation procedure.

Nucleation

Nielsen has given a summary of nucleation phenomena in crystallization of salts from solution in his lecture. He showed that at high enough supersaturation nucleation can be homogeneous. However, it usually is heterogeneous, occurring on impurity particles or the walls of the containing vessel, as is shown by the variable number density of crystals resulting from different methods of mixing solutions and the care taken to clean vessels.

Turnbull⁴ has shown that nucleation of barium sulfate crystals from dilute solution occurs rapidly compared to the rate of their growth, and that the number of growing crystals is constant with time. Probably most insoluble salts nucleate this way from dilute solution. The rate of nucleation is exponentially dependent upon supersaturation, so that there is essentially a critical supersaturation at which nucleation occurs on impurity particles in the solution.

Growth

The rate of growth of a crystal from solution can be controlled by diffusion of dissolved species through the solution or by the rate of incorporation of the species into the crystal (interface control). Mixed control is also possible. The parameter that indicates the type of control is RG/DC_0 , where R is the radius or other effective dimension, G is an interface growth coefficient defined below, D is the diffusion coefficient of the species in the solution, and C_0 is the equilibrium solubility of the crystal. When RG/DC_0 is large compared to unity the growth is controlled by diffusion in solution, whereas when it is small the growth is controlled by an interface process. Therefore, in order to measure the interface growth coefficient, the rate of growth of small crystals must be measured.

When the crystal growth is controlled by a surface or interface process, the flux of material that is deposited on unit surface area of a growing crystal per unit time is:

$$J = GS^n \quad (1)$$

where G is an interface growth coefficient defined by this equation, n is the order of the growth process, and S is the supersaturation:

$$S = \frac{C_m - C_0}{C_0}$$

where C_m is the actual concentration in solution of material depositing on the crystal.

The crystal growth of a number of slightly soluble salts in water has been measured under conditions of interface control. Table I lists the results for the order n of the growth process. From the table one can deduce that n depends on at least two factors, the stoichiometry of the crystallizing salt and its supersaturation, as deduced previously⁶. The results of Salomon¹² are particularly interesting in this regard, since he studied the growth rate of strontium sulfate crystals over a wide range of supersaturation, and observed their morphology under the microscope as well. Salomon found that the morphology of the crystals was quite different at high and low supersaturation, and that these differences correspond to the change in order from 2 to 3. It seems likely, therefore, that the change of order results from the nucleation of crystals with different crystallographic faces, and that the growth mechanisms on different faces is different. Further work is needed to clarify and confirm this relation between growth mechanism and morphology.

TABLE I
Order of Growth Laws for the Precipitation of Ionic Crystals

Salt	Supersaturation		References
	Low	High	
Silver Chloride	2		5, 10
Barium Sulfate	2	3 (4?)	2, 4, 6, 9, 11
Strontium Sulfate	2	3	6, 12, 13, 14
Lead Sulfate	2		15
Magnesium Oxalate	2		16
Silver Chromate	3	4	17, 18

To calculate the interface growth coefficient G of Eq. 1 from the rate of precipitation of a suspension of crystals it is necessary to know the size of the crystals. In the seed crystal experiments of Davies and Nancollas and their collaborators the crystals were large enough to observe in the microscope. In my own work the simultaneous measurement of conductivity and light scattering provided information to estimate the particle size and therefore to calculate G^9 . Calculations of G for various crystal growth experiments are given in Table II. The agreement between G measured for barium sulfate in my experiments and those of Nancollas and Purdie on seed crystals, notwithstanding the difference in reaction order, is noteworthy. The agreement between two different sets of experiments on silver chloride, done in quite different ways, also shows the usefulness of comparing G values. The value of G was not a function of supersaturation except in magnesium oxalate, where the value at higher supersaturation is probably too high because of nucleation of additional crystals. It would be interesting to obtain more accurate results for G on a wide variety of salts to see if it is related to such factors as ion size, ion polarizability, hydration, and other factors. In any event it appears that G , the rate of growth at unit supersaturation, is the correct parameter to compare for different conditions of precipitation.

TABLE II
Interface Growth Coefficient for Various Crystals

Salt	Super-saturation	Order n	G_2 moles/cm ² -sec.	References
Barium Sulfate	2	2	3×10^{-13}	11
	14	3	3×10^{-13}	9
Silver Chloride	low	2	3×10^{-11}	5
	low	2	3×10^{-11}	10
Magnesium Oxalate	.36	2	4×10^{-13}	16
	1.3	2	10^{-11}	16
Strontium Sulfate	9	3	3×10^{-12}	20

A number of different theories have been proposed for interface controlled growth from solution³⁻⁸. Features such as surface diffusion, surface reactions including dehydration, surface defects such as emergent dislocations, surface steps and kinks in the steps, step spacing, surface roughness, impurity adsorption, and others are involved in these theories. To test most of these ideas more detailed study of the crystal surface itself during growth is required.

Coagulation

There are different indications that very small crystals often coagulate during their growth.

The light scattering results in Fig. 1 suggest that after about 18 minutes of growth the crystals begin to coagulate together to form larger crystals, which subsequently sediment to the bottom of the vessel containing them. The larger crystals have a lower scattering cross-section per unit volume

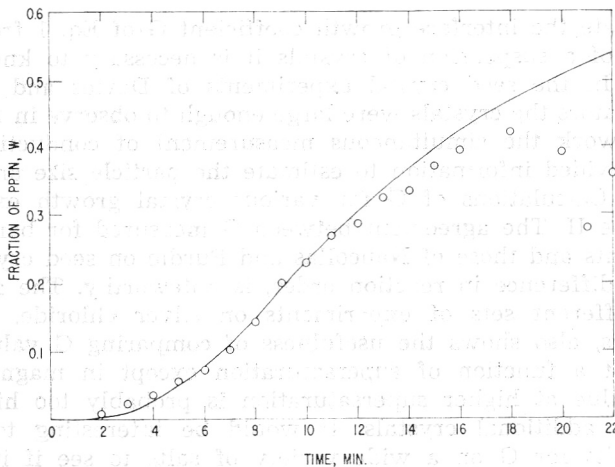


Fig. 1. Light scattering from growing barium sulfate crystals. Solutions of $\text{Ba}(\text{NO}_3)_2$ and K_2SO_4 were mixed to give a final BaSO_4 concentration of 1.6×10^{-7} moles/cm². The curve, showing the fraction of precipitation as a function of time, was found from conductivity measurements. The points are the intensity of scattered light normalized with the curve at $N = 0.1$.

than do the smaller particles, so that as coagulation proceeds the scattering actually decreases, as shown in Fig. 1. As the particles sediment the scattering also decreases until there are few particles in the scattering volume. After precipitation of slightly soluble salts a deposit often is found in the reaction vessel, consistent with this view.

The coagulation of smaller particles into larger ones gives a somewhat smaller effective area for deposition. The area of these larger particles is increased only very slightly with further deposition of material, giving the appearance in the kinetics of a constant growth area. Thus the deviations from the growth curves for various crystals pointed out previously^{6,9} give further evidence for coagulation. In the earlier stages the rate of growth increased proportional to the surface area of the crystals, but after the deviations the rate data behaved as if the area for deposition of material was constant.

Meehan and Miller also concluded that coagulation was occurring in their study of rapid precipitation of silver bromide¹⁰. Because of the possibility of coagulation, any study of nucleation rates and crystal sizes in precipitation from counts or observation of crystals after a certain time of crystallization is questionable. For example, the original precipitation »laws« of von Weimarn were deduced from observations of this sort; it seems likely that the results were often affected by coagulation. It is essential that investigators who use this observation technique give good evidence that coagulation has not occurred before conclusions can be drawn from such observations.

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IZVOD

Taloženje i rast kristala iz otopina

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Taloženje kristala iz otopina uključuje nukleaciju koja je obično heterogeni brzi proces, te naknadni rast kristala. U proučavanju kinetike površinskog procesa rasta kristala potrebno je mjeriti njihovu veličinu kao i brzinu uključivanja mate-

rijala iz otopine u kristal. Samo kod vrlo malih kristala moguće je održati površinski kontrolirani proces.

Za slabo topljive soli eksponent u jednadžbi transporta za proces rasta ovisi kako o stehiometriji soli, tako i o presičenju otopine. S druge strane, koeficijent površinskog rasta ovisi samo o vrsti kristala, a ne o stupnju presičenja otopine. U tablicama su navedeni numerički podaci za eksponent i za koeficijent površinskog rasta raznih kristala.

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